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CHEMICAL ANALYSIS OF LEAD AND ITS COMPOUNDS

Chemical Analysis of Lead and Its Compounds

BY

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Second Edition

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THE EAGLE-PICHER LEAD COMPANY

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THE EAGLE-PICHER LEAD COMPANY

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Raymond P. Way
4-16-1926

DEDICATED TO

Oliver S. Picher

who died April 26, 1920, and who was the first president of The Eagle-Picher Lead Company. His constant aim throughout life was the development of the lead industry. Its present state of perfection is largely due to his efforts at all times to advance the metallurgical art, as it relates to the manufacture of lead and its compounds, not only from a humanitarian standpoint, but also as a growth along sound scientific lines. In his death the industry has suffered a distinct loss.

PREFACE TO SECOND EDITION.

The demand for this book has made the Second Edition necessary. The book continues to be a compilation of standard methods, already well known, that combine accuracy with rapidity.

Certain revisions and additions have been made that should increase the usefulness of the book. A method of calculating percentage of composition of Sublimed White Lead by J. A. Schaeffer and a rapid method for analysis of copper and iron in red lead and litharge by B. S. White are also included.

March, 1922.

PREFACE.

A review of the literature on the analysis of lead and its compounds reveals a multiplicity of methods, many of which are of little value in technical work of today, owing to the many operations entailed and the possibility of error attending every lengthy analysis. The laboratory of today, so closely connected with all lines of manufacture, must control through chemical analysis every process leading from the raw material to each finished product. It demands extreme accuracy coupled with rapidity of manipulation. That the best methods combining these salient points are not in general use in many laboratories dealing with lead compounds is evidenced from the numerous requests for such which continually reach us.

It is with the hope that the methods adopted by the leading laboratories in the lead districts, will prove of some special value, that this work is written. In it will be found certain new methods which retain exactness with considerable conservation of time and many others of general adoption. Should it aid in increasing the efficiency of any laboratory practice the authors will feel that its mission has been fulfilled.

August, 1912.

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CHEMICAL ANALYSIS OF LEAD AND ITS COMPOUNDS

CHAPTER I

ANALYSIS OF LEAD ORES

The principal ore of lead which will be encountered by the analyst is Galena, the sulphide of lead, PbS. In certain instances Anglesite, the sulphate of lead, $PbSO_4$, and Cerrusite, the carbonate of lead, $PbCO_3$, will reach the laboratory for examination. The constituents usually sought in the analysis of these compounds are lead, zinc and silver, though at times the iron and silicates present must be determined. The value of the ore, however, will depend upon the content of lead, zinc and silver.

The ore upon reaching the laboratory is dried at 105° C. for several hours and then pulped so as to pass through a 100-mesh sieve. The ore is then ready for examination.

Ammonium Molybdate Method for the Determination of Lead

Digest one gram of the sample with 15 c.c. of concentrated nitric acid in a covered beaker. Boil the solution until the brown fumes of the oxides of

nitrogen have disappeared. Add 6 c.c. of concentrated sulphuric acid and again boil until the heavy fumes of sulphuric acid are evolved. Allow the solution to cool, add 30 c.c. of water and boil. Remove the beaker from the hot plate and allow the solution to stand at least four hours, preferably over night. Filter the solution, washing the precipitate by decantation three or four times to completely remove the iron. The filtrate is reserved for the determination of zinc.

Wash the filter paper used in the previous filtration with 75 c.c. of acid ammonium acetate solution made up in the following manner:

Ammonium hydroxide (concentrated)	95 c.c.
Water	100 c.c.
Acetic acid (80%)	125 c.c.

Follow this washing with 75 c.c. of hot water, allowing all the washings to be caught in the beaker containing the residual lead sulphate. Boil until complete solution has been effected and determine the lead volumetrically in the hot solution by titration with standard ammonium molybdate solution, as given under the Standardization of Ammonium Molybdate.

Standardization of Ammonium Molybdate

Dissolve 8.67 grams of ammonium molybdate in one liter of water. Each c.c. of this solution should be equivalent to one per cent of lead, when a one

gram sample is used. Standardize as follows: Weigh up 0.5 gram pure litharge. Add 30 c.c. hot water and 32 c.c. (80%) acetic acid. Heat to boiling and when all the litharge is in solution add 27 c.c. con. ammonium hydroxide. Dilute to 200 c.c. with hot water, boil and titrate with the standard ammonium molybdate, using an outside indicator of 1 part of tannic acid in 300 parts of water. The appearance of a yellow color indicates an excess of ammonium molybdate. It has been found that a correction of 0.7 of 1 c.c. of the titration volume must be deducted as a blank to allow for the sensitiveness of the reaction.

The following precautions must be observed in carrying out this method:

Calcium forms a more or less insoluble molybdate, and when calcium is present results are apt to be high. However, when less than 2 per cent of calcium and a high percentage of lead are present, there appears to be no interference from the calcium. This method is only applicable to samples containing more than 20 per cent of lead. Should a lower percentage of lead be present it may be determined by the bichromate method or weighed as the sulphate.

Bichromate Method for the Determination of Lead

Treat one gram of the sample with concentrated nitric acid, evaporate to dryness and cool. Take

up the residue with 75 c.c. of a solution made up in the following manner:

Acetic acid (80%)	255 c.c.
Ammonium hydroxide (concentrated)	150 c.c.
Water	595 c.c.

Boil gently for a short time, filter, and wash well with boiling water. Treat the filtrate with sufficient neutral potassium bichromate to precipitate all the lead and boil until the lead chromate has become an orange yellow color. Filter and wash with hot water until all the uncombined potassium bichromate is removed. The above conditions must be carefully watched, as a slight deviation may result in the formation of a basic lead chromate. The ready formation of this compound has prevented the general adoption of this method. Dissolve the lead chromate in dilute hydrochloric acid (1:1), using as little of the acid as possible.

Titrate the chromic acid present in the solution with ferrous ammonium sulphate, having an iron value of 0.00202, using a two per cent solution of potassium ferricyanide as an outside indicator. It is necessary to deduct 0.5 of one c.c. of the ferrous ammonium sulphate standard solution for each 75 c.c. of solution used, as the amount required for the sensitiveness of the reaction.

To prepare the ferrous ammonium sulphate solution dissolve 14.19 grams c. p. ferrous ammonium sulphate in a liter of distilled water. A small scrap of aluminum foil in the bottle prevents oxidation.

Calculation

The percentage of lead may be determined directly by multiplying the number of c.c. of ferrous ammonium sulphate used by the factor 0.25. This factor is determined by the following equations:

$K_2Cr_2O_7 + 6\ Fe\ SO_4 + 8H_2SO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7\ H_2O.$

$2\ PbCrO_4 = 2\ Pb + Cr_2O_6.$

$Cr_2\ O_6$ is equivalent to 6 Fe.

2 Pb is equivalent to 6 Fe.

Therefore the factor from iron to lead equals $\frac{414.60}{335.04} = 1.237$

Strength of ferrous ammonium sulphate solution equals 0.00202 Fe.

$0.00202 \times 1.237 = 0.0025$ equals grams of lead per c.c. of solution.

Then the number of c.c. of ferrous ammonium sulphate used multiplied by 0.25 or divided by 4 gives the percentage of lead present when a one gram sample is used.

The lead may be calculated directly from the amount of iron titrated by using the factor 1.237.

Sulphate Method for the Determination of Lead

Details for the gravimetric determination of lead as sulphate are given under the analysis of Basic Carbonate of Lead on page 89.

Determination of Zinc

Add 8 grams of ammonium chloride to the filtrate and washings from the lead sulphate precipitate. Render the solution alkaline with ammonium hydroxide, boil, filter off any iron hydroxide which is precipitated, wash, dissolve this precipitate in dilute hydrochloric acid, reprecipitate with ammonium hydroxide, boil, filter and thoroughly wash. Combine the filtrates, neutralize the ammonium hydroxide present with hydrochloric acid and add an excess of 6 c.c. of concentrated hydrochloric acid. Dilute to about 250 c.c., heat to about 80° C., add a few drops of saturated sodium thiosulphate solution. Titrate with standard potassium ferrocyanide as outlined under the Standardization of Potassium Ferrocyanide, using as an outside indicator a 5 per cent uranium nitrate solution.

Standardization of Potassium Ferrocyanide

Dissolve 10 grams of pure metallic zinc in hydrochloric acid. The solution is made up to 1 liter and a volume equivalent to 0.2 gram is measured out. The remaining solution may be kept for restandardizing the ferrocyanide solution which, on standing, appears to change from time to time. In place of using the standard zinc solution, 0.5 gram of pure zinc oxide may be used for each standardization.

The ferrocyanide solution is made by dissolving 43.26 grams of crystallized potassium ferrocyanide and 7 grams of sodium sulphite in a liter of water. The addition of the sodium sulphite helps to keep

the ferrocyanide solution at a constant strength. One c.c. of this solution will be equal to approximately 0.01 gram of metallic zinc.

The indicator is prepared by dissolving uranium nitrate in water until a faint yellow color is produced. A 5 per cent solution will usually give a good end reaction.

The acid solution containing 0.2 of a gram of zinc is made faintly alkaline with ammonium hydroxide, using litmus paper to determine the end point. Reacidify faintly with hydrochloric acid and add 6 c.c. of concentrated hydrochloric acid in excess. Dilute to about 250 c.c. and heat to about 80° C.

The solution is titrated with the ferrocyanide solution until a few drops of the zinc solution give a brownish tinge to the uranium nitrate indicator on the spot plate. As the end point develops slowly, it is well to examine each spot after standing for a brief time. The first one developing a brown tinge is taken as the end point. It is necessary to make a correction for the amount of ferrocyanide solution required to develop a brown color in the uranium nitrate indicator when zinc is absent. This correction is deducted from the total amount of ferrocyanide solution used and will usually run about 0.5 of a c.c.

Determination of Silver

The treatment of lead ores for the assay of silver depends wholly upon the nature of the ore. The various fluxes used for the formation

of the lead button cannot be outlined here, owing to their number; the analyst desiring to make this determination may readily determine a method of reduction by consulting any standard text on assaying.

CHAPTER II

SUBLIMED WHITE LEAD

(Basic Sulphate of Lead)

An average approximate analysis of sublimed white lead as commercially placed upon the market should show about 78.5 per cent of lead sulphate, 16 per cent of lead oxide and 5.5 per cent of zinc oxide.

Analysis

Total Sulphates

Mix 0.5 gram of the sample with 3 grams of sodium carbonate in a beaker. Treat the mixture with 30 c.c. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute the contents of the beaker with hot water, filter off the residue and wash until the filtrate is about 200 c.c. in volume. Reject the residue. By this reaction all the lead sulphate is changed to carbonate, the sulphate being transposed into sodium sulphate, which is found in the filtrate.

Acidulate the filtrate with hydrochloric acid and add an excess of about 2 c.c. of the acid. Boil, and add a slight excess of barium chloride solution (12 c.c. of an 8 per cent solution). When the precipitate has well settled, 4 hours or preferably over night, filter on an ashless filter, wash, ignite and weigh as $BaSO_4$. Calculate the $BaSO_4$ to

$PbSO_4$ by using the factor 2.6, when a half gram sample is used.

Weight of $BaSO_4 \times 1.3$ equals weight $PbSO_4$.

On 0.5 gram sample factor $BaSO_4$ to $PbSO_4$=2.6.

Lead

Molybdate Method[1]

Dissolve 1 gram of the sample in 100 c.c. of an acid ammonium acetate solution made up as follows:

Eighty per cent acetic acid	125 c.c.
Concentrated ammonium hydroxide	95 c.c.
Water	100 c.c.

Add this solution hot and dilute with about 50 c.c. of water. Boil until dissolved.

Dilute to 200 c.c. and titrate with standard ammonium molybdate solution, spotting out on a freshly prepared solution of tannic acid. Details of this method are given under the Analysis of Lead Ores.

Ammonium molybdate is a slightly variable salt, but a solution containing 8.67 grams per liter usually gives a standard solution:

1 c.c. equals 0.01 gram Pb.

Standardize against pure PbO or pure $PbSO_4$.

Bichromate Method

Treat the sample as above described until dissolved. If the solution is not quite clear, filter.

[1]Modification of Low's Method. Technical Methods of Ore Analysis, Low, p. 149.

Add to the filtrate an excess of neutral potassium bichromate solution. Boil until the lead chromate has become an orange yellow color and stand in a warm place until the precipitate has settled. Filter on a Gooch crucible, wash thoroughly, ignite below a red heat and weigh as $PbCrO_4$.

The $PbCrO_4$ may be estimated volumetrically by titrating the chromic acid present. For this method, dissolve the lead chromate from off the filter with hydrochloric acid. Wash well and determine the chromic acid present with a standard solution of ferrous ammonium sulphate, using a dilute solution of potassium ferricyanide as an outside indicator. The ferrous ammonium sulphate is made up of such strength that 1 c.c. will equal 0.00202 gram Fe. For a one gram sample divide the number of c.c. of ferrous ammonium sulphate used by 4.

Details of this calculation are given under the Analysis of Lead Ores.

Deduct the lead found as lead sulphate from the total lead and calculate the residual lead to PbO.

Zinc[1]

Boil one gram of the sample in a beaker with the following solution:

Water	30 c.c.
Ammonium chloride	4 grams.
Concentrated hydrochloric acid	6 c.c.

[1]Low's Technical Methods of Ore Analysis.

If the sample is not quite dissolved the result is not affected, as the residue is lead sulphate or precipitated lead chloride.

Dilute to 200 c.c. with hot water, add 2 c.c. of a saturated sodium thiosulphate solution and titrate with a standard solution of potassium ferrocyanide, spotting out on a 5 per cent solution of uranium nitrate as outlined under the Analysis of Lead Ores. Calculate the zinc to zinc oxide by multiplying by the factor 1.245.

Iron Oxide

Determine this constituent as outlined under the Analysis of Litharge.

U. S. Interdepartmental Committee's Recommended Specification for Basic Sulphate White Lead, Dry and Paste[1]

1. General

Basic sulphate white lead may be ordered in the form of dry pigment or paste ground in linseed oil. Material shall be purchased by net weight.

(a) Dry Pigment

The pigment shall be the sublimed product prepared from lead sulphide ores, free from impurities and adulterants, and shall meet the following requirements:

[1]Prepared and recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization, September 22, 1919. P. H. Walker, Bureau of Standards, Chairman; H. E. Smith, U. S. Railroad Administration, Secretary. Circular of the Bureau of Standards. No. 85.

Color—Color strength: When specified shall be equal to that of a sample mutually agreed upon by buyer and seller.

Coarse particles[1]:	Min.	Max.
Retained on standard No. 200 screen.....	....	None.
Retained on standard No. 325 screen...per cent..	....	0.5
Composition:		
Lead oxide .....do....	11.0	18.0
Zinc oxide .....do....	....	9.0
Total impurities, including moisture.....do....	....	1.0

The remainder shall be lead sulphate.

(b) Pastes

The paste shall be made by thoroughly grinding the dry pigment with pure raw or refined linseed oil.

The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. It shall mix readily in all proportions without curdling with linseed oil, turpentine, or volatile mineral spirits or any combination of these substances.

The paste shall consist of:

	Min.	Max.
Pigment .....per cent..	89	91.0
Linseed oil.....do....	9	11.0
Moisture and other volatile matter.....do....	..	0.7
Coarse particles and "skins" (total residue retained on No. 325 screen, based on pigment).....per cent..	..	0.5

2. Sampling

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole.

[1]The No. 200 and No. 325 screens are the same as screens formerly known as 200 and 350 mesh.

With the dry pigment, this package shall be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory; and when this is for any reason not done, the inspector shall determine, by thorough testing with a paddle or spatula, whether the material meets the requirement regarding not caking in the container. (See 4*a*.) After assuring himself that the paste is not caked in the container the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

Samples will in general be tested by the following methods, but the purchaser reserves the right to apply any additional tests, or use any available information to ascertain whether the material meets the specification.

3. Laboratory Examination of Dry Pigment

(a) Color

Take 1 gram of the sample, add 10 to 12 drops linseed oil, rub up on a stone slab or glass plate

with a flat bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner, 1 gram of the standard basic sulphate white lead. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as white as or whiter than the "standard," it passes this test. If the "standard" is whiter than the sample, the material does not meet the specification.

(b) Color Strength

Weigh accurately 0.01 gram of lampblack, place on a large glass plate or stone slab, add 5 drops of linseed oil and rub up with a flat bottomed glass pestle or muller, then add exactly 10 grams of the sample and 45 drops of linseed oil and grind with a circular motion of the muller 50 times; gather up with a sharp edged spatula and grind out twice more in a like manner, giving the pestle a uniform pressure. Treat another 0.01 gram of the same lampblack in the same manner except that 10 grams of standard basic sulphate white lead is used instead of the 10 grams of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light as or lighter in color than the "standard," it passes this test. If the "standard" is lighter in color than the sample, the material does not meet the specification.

(c) Coarse Particles

Dry in an oven at 105 to 110° C. a No. 200 and a No. 325 sieve, cool, and weigh accurately. Weigh

100 grams of the sample, dry at 100° C.; transfer to a mortar, add 100 c.c. kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene first through the 200 and then through the 325 sieve, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles too coarse to pass the sieves have been washed through, wash all kerosene from the sieves with ether or petroleum ether, heat the sieves for one hour at 105 to 110° C., cool, and weigh. The increase in weight of the No. 200 sieve should be not more than 0.010 gram, and of the No. 325 sieve not more than 0.500 gram.

(d) Qualitative Analysis

Test for matter insoluble in acid ammonium acetate solution, for calcium, for carbonates, and for any other impurities suspected by the regular methods of qualitative analysis.

(e) Moisture

Place one gram of the sample in a tared, wide mouth, short weighing tube provided with a glass stopper. Heat with stopper removed for 2 hours at a temperature between 100 and 105° C. Insert stopper, cool, and weigh. Calculate loss in weight as moisture.

(f) Insoluble Impurity and Total Lead

In a 250-c.c. beaker, moisten 1 gram of the pigment with a few drops of alcohol; add 50 c.c. of acid ammonium acetate solution. (See reagents 5*a*.) Heat to boiling and boil for 2 minutes. Decant through a filter paper, leaving any undecor

posed matter in the beaker. To the residue in the beaker, add 50 c.c. of the acid ammonium acetate solution, heat to boiling, and boil for 2 minutes. Filter through the same paper and wash with hot water. If an appreciable residue remains, ignite and weigh as insoluble impurity. Unite the acid ammonium acetate solutions, heat to boiling, and add dropwise, with stirring, a slight excess (in total about 10 to 15 c.c.) of dichromate solution. (See reagents 5*b*.) Heat until the precipitate assumes an orange color, let settle, filter on a weighed Gooch crucible, wash by decantation with hot water until the washings are colorless, and finally transfer all of the precipitate to the crucible. Then wash with 10 c.c. of 95 per cent ethyl alcohol and finally with 10 c.c. of ethyl ether. Dry at 110 to 120° C., cool, and weigh $PbCrO_4$. Calculate to PbO by multiplying by the factor 0.69.

(g) Zinc Oxide

Weigh accurately about 1 gram of the pigment, transfer to a 400-c.c. beaker, add 30 c.c. of HCl (1:2), boil for 2 or 3 minutes, add 200 c.c. of water and a small piece of litmus paper, add NH_4OH until slightly alkaline, render just acid with HCl, then add 3 c.c. of concentrated HCl, heat nearly to boiling, and titrate with standard potassium ferrocyanide as in standardizing that solution. (See reagents 5*d*.) Calculate total zinc as ZnO.

(h) Lead Sulphate

Treat 0.5 gram of the pigment in a 400-c.c. beaker with a few drops of alcohol, add 10 c.c. of bromine

water, 10 c.c. HCl (1:1), and 3 grams of NH_4Cl. Cover with a watch glass and heat on a steam bath for 5 minutes, add hot water to give a total volume of about 200 c.c., boil for 5 minutes, filter to separate any insoluble matter (a pure pigment should be completely dissolved), and wash thoroughly with hot water. (The insoluble matter may be ignited, weighed, and examined qualitatively.) Neutralize the clear solution (original solution or filtrate from insoluble matter) in a covered beaker with dry Na_2CO_3, add 1 gram more of dry Na_2CO_3, and boil 10 to 15 minutes. Wash off cover, let settle, filter, and wash with hot water. Redissolve the precipitate in HCl (1:1), reprecipitate with Na_2CO_3 as above, filter, and wash thoroughly with hot water. Acidify the united filtrates with HCl, adding about 1 c.c. in excess. Boil to expel bromine, and to the clear boiling solution add slowly with stirring 15 c.c. of barium chloride solution. (See reagents 5*e*.) Let stand on steam bath for about 1 hour, filter on a weighed Gooch crucible, wash thoroughly with boiling water, dry, ignite, cool, and weigh as $BaSO_4$. Calculate to $PbSO_4$, using the factor 1.3.

(i) Calculations

Calculate the percentage of $PbSO_4$ to PbO by multiplying by the factor 0.736 and subtract the result from the percentage of PbO found under (*f*); report the difference as PbO. Report ZnO found under (*g*) as percentage of ZnO. Moisture and insoluble matter are reported as such.

4. Laboratory Examination of Paste

(a) Caking in Container

When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of white lead paste. The paste shall be finally thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out from it.

(b) Mixing with Linseed Oil

One hundred grams of the paste shall be placed in a cup, and 30 c.c. of linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(c) Moisture and Other Volatile Matter

Weigh accurately from 3 to 5 grams of the paste into a tared flat bottomed dish, about 5 cm. in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for 1 hour, cool, and weigh. Calculate loss in weight as percentage of moisture and other volatile matter.

(d) Percentage of Pigment

Weigh accurately about 15 grams of the paste into a weighed centrifuge tube. Add 20 to 30 c.c.

of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 c.c. in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 c.c. of extraction mixture and once with 40 c.c. of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for 2 hours. Cool, weigh, and calculate the percentage of pigment.

(e) Examination of Pigment

Grind the pigment from (*d*) to a fine powder, pass through a No. 80 screen to remove any "skins," preserve in a stoppered tube, and examine as under 3(*a*), 3(*b*), 3(*d*), 3(*f*), 3(*g*), 3(*h*), and 3(*i*), Laboratory Examination of Dry Pigment.

(f) Preparation of Fatty Acids

To about 25 grams of the paste in a porcelain casserole, add 15 c.c. of aqueous sodium hydroxide (see reagents), and 75 c.c. of ethyl alcohol, mix, and heat uncovered on a steam bath until saponification is complete (about 1 hour). Add 100 c.c. of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 c.c. will usually suffice),

boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and $PbSO_4$ precipitate, wash once with water, then add 50 c.c. of water and 50 c.c. of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 c.c. portion of water and then with 5 c.c. portions of water until free from sulphuric acid. Then draw off completely the water layer. Transfer the ether solution to a dry flask, add 25 to 50 grams of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100 c.c. Erlenmeyer flask. Pass a rapid current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off. The fatty acids prepared as above should be kept in a stoppered flask and examined at once.[1]

[1]It is important to follow all of the details since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

(g) Test for Mineral Oil

Place 10 drops of the fatty acid (*f*) in a 50-c.c. test tube, add 5 c.c. of alcoholic soda (see reagents), boil vigorously for 5 minutes, add 40 c.c. of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear the oil is not pure linseed oil.

(h) Iodine Number of Fatty Acids

Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker and weigh accurately. Transfer by dropping about 0.15 gram (0.10 to 0.20 gram) to a 500-c.c. bottle having a well ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 c.c. of chloroform and whirl the bottle to dissolve the sample. Add 10 c.c. of chloroform to each of two empty bottles like that used for the sample. Add to each bottle 25 c.c. of the Hanus solution (see reagents 5*k*) and let stand with occasional shaking for one-half hour. Add 10 c.c. of the 15 per cent potassium iodide solution and 100 c.c. of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titration on the two blank tests should agree within 0.1 c.c. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is

centigrams of iodine to 1 gram of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(i) Coarse Particles and "Skins"

Weigh out an amount of paste containing 100 grams of pigment (see *d*), add 100 c.c. of kerosene, wash through No. 325 screen, and weigh the residue as in 3 (*c*). The total residue left on the screen should be not more than 0.5 gram.

5. Reagents

(a) Acid Ammonium Acetate Solution

Mix 150 c.c. of 80 per cent acetic acid, 100 c.c. of water, and 95 c.c. of strong ammonia (specific gravity 0.90).

(b) Dichromate Solution

Dissolve 100 grams sodium dichromate ($Na_2Cr_2O_7.2H_2O$) or potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1000 c.c.

(c) Uranyl Indicator for Zinc Titration

A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(d) Standard Potassium Ferrocyanide

Dissolve 22 grams of the pure salt in water and dilute to 1000 c.c. To standardize, transfer about 0.2 gram (accurately weighed) of pure metallic zinc or freshly ignited pure ZnO to a 400-c.c. beaker. Dissolve in 10 c.c. of HCl and 20 c.c. of

water. Drop in a small piece of litmus paper, add NH_4OH until slightly alkaline, then add HCl until just acid and finally add 3 c.c. of strong HCl. Dilute to about 250 c.c. with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing 1 minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtain when the sample is titrated.

(e) Barium Chloride Solution

Dissolve 100 grams of pure crystallized barium chloride in water and dilute to 1000 c.c.

(f) Standard Sodium Thiosulphate Solution

Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from CO_2 in the proportion of 24.83 grams of crystallized sodium thiosulphate to 1000 c.c. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. II, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact

iodine value, rather than to attempt to adjust it to exactly decinormal strength. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(g) Starch Solution

Stir up 2 to 3 grams of potato starch or 5 grams of soluble starch with 100 c.c. of 1 per cent salicylic acid solution, add 300 to 400 c.c. of boiling water, and boil the mixture until the starch is practically dissolved; then dilute to 1 liter.

(h) Extraction Mixture

Mix 10 volumes ether (ethyl ether), 6 volumes benzol, 4 volumes methyl alcohol, and 1 volume acetone.

(i) Aqueous Sodium Hydroxide

Dissolve 100 grams of NaOH in distilled water and dilute to 300 c.c.

(j) Potassium Iodide Solution

Dissolve 150 grams of potassium iodide free from iodate in distilled water and dilute to 1000 c.c.

(k) Hanus Solution

Dissolve 13.2 grams of iodine in 1000 c.c. of glacial acetic acid, 99.5 per cent, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 c.c. of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(l) Alcoholic Sodium Hydroxide Solution

Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 grams per 1000 c.c. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 grams to 1000 c.c.) kept at about 50° C. for 15 days, and then distilled.

CHAPTER III

THE LEAD CONTENTS IN SUBLIMED WHITE LEAD—A CALCULATION[1]

The composition of sublimed white lead, the basic sulphate of lead, has become a most important factor to users of this pigment. Both among rubber manufacturers and producers of paints, it is being found essential that the contents of lead oxide and lead sulphate be known, so that advantage may be fully taken of its characteristic properties. This control necessitates an analysis of the compound in the laboratory.

In analyzing sublimed white lead by the usual method, it is found that the percentage composition can be determined only by an analysis entailing lengthy manipulation, in which the content of lead oxide is directly dependent upon the accuracy of the other determinations, owing to the necessity of estimating its percentage by a calculation based upon the percentage of the other constituents present. The steps in the procedure must therefore be closely watched for slight inaccuracies at all times.

As is well known, the average composition of sublimed white lead is given as follows:

Lead sulphate	78.5
Lead oxide	16.0
Zinc oxide	5.5

[1] J. Ind. & Eng. Chem., 6, 200 (1914).

That its composition varies only slightly from the above analysis during a long period of time, is shown by its comparison with an average of the entire output of the Eagle-Picher Lead Company extending over five months' time, an average embracing 270 total analyses.

This average shows the composition to be:

Lead sulphate.....	76.68
Lead oxide.....	17.23
Zinc oxide.....	5.79
	99.70

A slightly higher lead oxide and zinc oxide content and a correspondingly lower lead sulphate content is found, than in the usually stated formula. It shows, however, only slight variation. The average total percentage, consisting of lead sulphate, lead oxide, and zinc oxide, was found to be 99.70 per cent. The remaining 0.3 of a per cent is only rarely determined, and when actually sought is found to consist of moisture, occluded gas and ash. A definite ratio exists between the total lead content and the lead sulphate and lead oxide contents, and advantage may be taken of this relation for a rapid and accurate determination of the lead constituents in sublimed white lead.

In order to arrive at the short method for the analysis which is based upon a direct calculation of the lead and zinc contents, it is necessary that only the percentage of zinc and lead be determined by the methods already described.

Using the percentages of zinc oxide and total lead, together with the average total, 99.70 per cent, determined from the large number of analyses, the contents of lead oxide and lead sulphate are readily estimated by the following calculation:

Total percentage of lead compounds present equals 99.70 per cent (average) = total percentage found of ZnO, PbO and $PbSO_4$ less percentage ZnO.

Total percentage of lead compounds present equals 99.70 per cent (average total) minus percentage ZnO.

Atomic weight lead.....207.1
Molecular weight lead oxide.....223.1
Molecular weight lead sulphate.....303.1

As a hypothetical case, we can assume the presence of a 4.70 per cent ZnO and 69.00 per cent metallic lead.

$$(1)\quad \frac{\left(\frac{\text{Mol. wt. } PbSO_4}{\text{At. wt. Pb.}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\frac{\text{Mol. wt. } PbSO_4 - \text{mol. wt. PbO}}{\text{Mol. wt. PbO}}} = \%\ \text{PbO present}$$

$$(2)\quad \frac{\left(\frac{\text{Mol. wt. PbO}}{\text{At. wt. Pb}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\frac{\text{Mol. wt. PbO} - \text{Mol. wt. } PbSO_4}{\text{Mol. wt. } PbSO_4}} = \%\ PbSO_4\ \text{present}$$

Determining the percentage of lead oxide and lead sulphate present by the above formulas we find:

$$(1)\quad \frac{\left(\frac{303.1}{207.1} \times 69.00\right) - 95.00}{\frac{303.1 - 223.1}{223.1}} = \text{per cent PbO} = 16.68$$

$$(2)\quad \frac{\left(\frac{223.1}{207.1} \times 69.00\right) - 95.00}{\frac{223.1 - 303.1}{303.1}} = \text{per cent } PbSO_4 = 78.32$$

Therefore by substituting the percentages of lead and zinc oxide in the following formula which is derived from equation (1) the percentage of PbO in the sublimed white lead is easily found.

The sum of the percentages of zinc oxide and lead oxide subtracted from 99.7 gives the percentage of lead sulphate.

Per cent PbO = [1.464 × % Pb — (99.7 — % ZnO)] 2.79.

A comparison of the actual results obtained by the complete analysis of sublimed white lead and its calculated composition shows that the values obtained are concordant. Indeed the only essential factors for the short method are accurate determinations of the lead and zinc contents. The removal of several steps in the analysis leads to greater accuracy coupled with a considerable curtailment of time.

A table of comparisons shows the following concordance of results:

No.	Analysis	Lead sulphate	Lead oxide	Zinc oxide	Total lead	Total
1	Complete	79.20	15.28	5.23	68.30	99.72
	Calculated	79.17	15.30	....	.....	.....
2	Complete	77.74	16.81	5.11	68.70	99.66
	Calculated	77.97	16.62	....	.....	.....
3	Complete	77.09	16.95	5.73	68.40	99.77
	Calculated	76.85	17.12	....	.....	.....
4	Complete	80.20	14.66	4.86	68.40	99.72
	Calculated	80.15	14.69	....	.....	.....
5	Complete	78.00	16.60	5.11	68.70	99.71
	Calculated	77.97	16.62	....	.....	.....
6	Complete	77.84	17.10	4.86	69.00	99.80
	Calculated	77.69	17.15	....	.....	.....
7	Complete	77.22	16.20	6.23	67.80	99.63
	Calculated	77.41	16.06	....	.....	.....
8	Complete	74.10	20.21	5.48	69.40	99.79
	Calculated	74.00	20.22	....	.....	.....
9	Complete	77.63	15.92	6.23	67.80	99.78
	Calculated	77.41	16.06	....	.....	.....
10	Complete	76.05	17.93	5.73	68.60	99.71
	Calculated	76.04	17.93	....	.....	.....
11	Complete	76.98	17.78	4.98	69.10	99.74
	Calculated	76.85	17.87	....	.....	.....

That this method will prove of value will be readily appreciated by all chemists who have to determine the percentage composition of any basic sulphate of lead, either for the purpose of meeting specifications or for accurate control of finished products.

CHAPTER IV

SUBLIMED BLUE LEAD

Sublimed blue lead is at the present time finding its greatest value as an inhibitive pigment for the protection of iron and steel. The high rating given to this pigment on exposure tests conducted under the supervision of the American Society for Testing Materials for the prevention of corrosion is bringing it more and more to the attention of paint technologists and engineers.

In composition it consists of lead sulphate, lead sulphide, lead sulphite, lead oxide and zinc oxide, with occasional traces of carbon. Its color is a pleasing dull steel gray.

Analysis

Total Lead

The total lead content is determined volumetrically as outlined under the estimation of Lead in Lead Ores.

Total Sulphur

Treat one-half gram of the sample in a beaker with 10 c.c. of water and a few c.c. of bromine water. Boil gently until all the bromine has passed off. Dilute with water, add another portion of bromine water, boil and continue the treatment until the sediment has become white in color. Add

8 c.c. of nitric acid, evaporate the solution until the brown fumes of nitric acid have disappeared, dilute with water and add an excess of sodium carbonate. From this point proceed with the determination of the sulphate as outlined under Sublimed White Lead.

Lead Sulphate

On a separate sample determine the lead sulphate as outlined under Sublimed White Lead, by transposition of the sulphate with sodium carbonate.

Lead Sulphite

Boil one and one-half grams of the sample with 3 grams of sodium carbonate, allow to stand, filter and thoroughly wash. To the filtrate add 3 c.c. of bromine water, heat gently to oxidize the sodium sulphite to sulphate, acidify with HCl and precipitate the sulphate with barium chloride. Filter, wash and weigh in the usual manner. The barium sulphate formed will contain both the sulphur present as sulphate and that present as sulphite converted to sulphate. Deduct the amount present as sulphate and calculate the remainder to lead sulphite.

Lead Sulphide

Deduct the sulphur present as sulphate and sulphite from the total sulphur and report the difference as lead sulphide.

Lead Carbonate

A small amount of lead may be present as carbonate. Determine the carbonic acid present as outlined under Basic Carbonate White Lead, and calculate this carbonic acid to lead carbonate.

Lead Oxide

Deduct the lead present as lead sulphate, lead sulphite, lead sulphide and lead carbonate from the total lead and report the difference as lead oxide.

Zinc Oxide

Determine the zinc present as outlined under Sublimed White Lead, and report it as zinc oxide.

Carbon and Volatile Matter

Ignite the sample in a partially covered crucible at a low heat for two hours. Report the difference as carbon and volatile matter.

CHAPTER V

ZINC OXIDE

Zinc oxides are usually analyzed for zinc oxide, lead sulphate and water soluble. In addition to this certain physical properties are often examined and these tests often are as important as the chemical analysis. The usual physical tests made on pigments are found on page 148.

Analysis

Zinc Oxide

When high grade oxides containing more than 99% pure ZnO are to be analyzed it is best to obtain total impurities and report the ZnO by difference. Ordinarily, however, the zinc content should be determined as described on page 39.

Lead Sulphate

For leaded zincs having more than 20 per cent lead the method described for Sublimed White Lead, on page 10, should be used. For all others weigh up a one gram sample and proceed by the Bichromate Method as described on page 10. The percentage lead times 1.464 equals percentage lead sulphate.

Water Soluble

Since the water soluble material in zinc oxide is practically all zinc sulphate the following method has been found quite accurate and considerably shorter than the methods usually employed.

Weigh up 5 grams of the sample and pour it into a beaker containing 200 c.c. boiling hot water. Stir the suspension vigorously for one minute without further boiling and allow the zinc oxide to settle. Filter the supernatant liquor into a clean beaker taking great care not to allow any of the milky liquor to spatter into the beaker with the filtrate. Wash the zinc oxide onto the filter paper with hot water, wash twice and allow to drain.

To the filtrate add 5 grams ammonium chloride, 6 c.c. concentrated hydrochloric acid and heat to boiling. Titrate hot with standard potassium ferrocyanide solution using ammonium molybdate as outside indicator. A blank should be run with 200 c.c. water, 5 grams ammonium chloride and 6 c.c. concentrated hydrochloric acid and this amount subtracted from values obtained with zinc oxide.

The factor converting zinc to zinc sulphate is 2.47.

Total Sulphur

Total sulphur may be determined by the method described on page 40. A 10 gram sample should be used.

U. S. Interdepartmental Committee's Recommended Laboratory Examination for Zinc Oxide, Dry and Paste[1]

1. Laboratory Examination, Dry Pigment

(a) Color

Take 5 grams of the sample, add 1.5 c.c. of linseed oil, rub up on a stone slab or glass plate with a flat bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 5 grams of the standard zinc oxide. Spread the two pastes side by side on a clear colorless glass plate and compare the colors. If the sample is as white as or whiter than the "standard," it passes this test. If the "standard" is whiter than the sample, the material does not meet the specification.

(b) Color Strength

Weight accurately 0.01 gram of lampblack, place on a large glass plate or stone slab, add 0.2 c.c. of linseed oil and rub up with a flat bottomed glass pestle or muller, then add exactly 10 grams of the sample and 2.5 c.c. of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp edged spatula and grind out twice more in a like manner, giving the pestle a uniform pressure. Treat another 0.01 gram of the same lampblack in the same manner except that 10

[1]Prepared and recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization, January 12, 1920. P. H. Walker, Bureau of Standards, Chairman; H. E. Smith, U. S. Railroad Administration, Secretary. Circular of the Bureau of Standards. No. 87.

grams of standard zinc oxide is used instead of the 10 grams of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light as or lighter in color than the "standard," it passes this test. If the "standard" is lighter in color than the sample, the material does not meet the specification.

(c) Coarse Particles

Dry in an oven at 105 to 110° C. a standard No. 200 brass or copper sieve, cool and weigh accurately. Weigh 50 grams of pigment which has been previously thoroughly dried by heating in an oven at 105 to 110° C. until all moisture is driven off. Transfer to a wide mouth bottle or cylinder of about 300 c.c. capacity, add about 200 c.c. of dry kerosene, stopper and shake vigorously for about 5 minutes. Remove stopper and wash back into the cylinder with a jet of kerosene any pigment adhering to the stopper. Pour about 50 c.c. of the kerosene with suspended pigment onto the sieve, let drain through and gradually transfer the whole of the kerosene and pigment to sieve, finally using a jet of kerosene to transfer the last of the pigment. With proper manipulation a large portion of the pigment will pass through the sieve during the process of transferring from the cylinder. When all pigment has been thrown on the sieve, wash with a jet of kerosene until no more pigment passes through. To make sure that all particles have been thoroughly washed through,

move the sieve from over the vessel in which the main portion of kerosene and pigment have been caught to over a clear glass dish resting on a black surface and wash all portions of the sieve with a jet of kerosene, using not less than 200 c.c. of kerosene. This kerosene caught in this dish should be entirely free from pigment. If any pigment can be seen in the liquid, repeat washing until at least 200 c.c. can be washed through without showing any pigment. Then wash with a jet of kerosene all pigment adhering to the frame of the sieve beneath the wire mesh. Finally wash the kerosene from the sieve with petroleum ether, dry at 105 to 110°, cool and weigh. The increase in weight should be not more than 0.01 gram.

(d) Qualitative Analysis

Test for matter insoluble in hydrochloric acid, for lead, calcium, etc., by regular methods of qualitative analysis.

(e) Zinc Oxide

With samples free from impurities (see (*d*)), ignite a weighed sample and calculate the residue as ZnO. With samples containing impurity, proceed as follows: Weigh accurately about 0.25 gram, transfer to a 400-c.c. beaker, moisten with alcohol, dissolve in 10 c.c. of hydrochloric acid and 20 c.c. of water and titrate with standard potassium ferrocyanide following the procedure used in standardizing this reagent. (See 3(*i*).)

(f) Total Sulphur

Weigh accurately about 10 grams of the sample. Moisten with a few drops of alcohol, add 5 c.c. of bromine water (saturated solution of bromine), then concentrated hydrochloric acid in excess, boil to expel bromine, and dilute to about 100 c.c. (Material complying with the specification should all go into solution; if insoluble matter remains, filter and examine by appropriate methods.) Make alkaline with ammonia, then just acid with hydrochloric acid, heat to boiling and add about 10 c.c. of hot barium chloride solution. (See reagents.) Let stand several hours (overnight), filter on a weighed Gooch crucible, wash thoroughly with hot water, dry, ignite, cool, and weigh the $BaSO_4$. Calculate to S ($BaSO_4 \times 0.1373 = S$).

2. Laboratory Examination, Paste

(a) Caking in Container

When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of zinc oxide paste. The paste shall be finally thoroughly mixed, removed from the container, the container wiped clean, and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(b) Mixing with Linseed Oil

One hundred grams of the paste shall be placed in a cup, 35 c.c. of linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(c) Moisture and Other Volatile Matter

Weigh accurately from 3 to 5 grams of the paste into a tared flat bottomed dish, about 5 cm. in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate loss in weight as percentage moisture and other volatile matter.

(d) Per Cent Pigment

Weigh accurately about 15 grams of the paste into a weighed centrifuge tube. Add 20 to 30 c.c. of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 c.c. in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until clear. Decant the clear supernatant liquid. Repeat the extraction twice with 40 c.c. portions of extraction mixture, and once with 40 c.c. of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C.

for 2 hours. Cool, weigh, and calculate percentage of pigment.

(e) Examination of Pigment

Grind the pigment from (*d*) to a fine powder, pass through a No. 80 sieve to remove any "skins," preserve in a stoppered tube and apply tests 1 (*d*), (*e*), and (*f*). If required, apply tests 1 (*a*) and (*b*) in comparison with a portion of pigment extracted from the standard paste in exactly the same manner as in extracting the sample.

(f) Preparation of Fatty Acids

To about 25 grams of the paste in a porcelain casserole add 15 c.c. aqueous sodium hydroxide (see reagents), and 75 c.c. of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 c.c. water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 c.c. will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer, wash once with water; then add 50 c.c. of water and 50 c.c. of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 c.c. portion of water and then with 5 c.c. portions of water until free from sulphuric acid. Then draw off completely the water layer. Transfer the ether solution to a dry flask,

and add 25 to 50 grams of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100-c.c. Erlenmeyer flask. Pass a rapid current of dry air (pass through $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

Note.—It is important to follow all of the details since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(g) Test for Mineral Oil and Other Unsaponifiable Matter

Place 10 drops of the fatty acid (*f*) in a 50-c.c. test tube, add 5 c.c. of alcoholic soda (see reagents), boil vigorously for 5 minutes, add 40 c.c. of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(h) Iodine Number of Fatty Acids

Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker. Weigh accu-

rately. Transfer by dropping about 0.15 gram (0.10 to 0.20 gram) to a 500-c.c. bottle having a well ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 c.c. of chloroform. Whirl the bottle to dissolve the sample. Add 10 c.c. of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 c.c. of the Hanus solution (see reagents) and let stand, with occasional shaking, for one-half hour. Add 10 c.c. of the 15 per cent potassium iodide solution and 100 c.c. of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 c.c. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 gram of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(i) Coarse Particles and "Skins"

Weigh an amount of paste containing 50 grams of pigment (see 2 (*d*)), add kerosene, and wash through a No. 200 screen as in 1 (*c*). The residue is reported as "Coarse particles and skins," and should weigh less than 0.25 gram.

Reagents

(a) Extraction Mixture

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(b) Aqueous Sodium Hydroxide

Dissolve 100 grams sodium hydroxide in distilled water and dilute to 300 c.c.

(c) Standard Sodium Thiosulphate Solution

Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 grams crystallized sodium thiosulphate to 1000 c.c. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Analytical Chemistry, Treadwell-Hall, vol. II, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(d) Starch Solution

Stir up 2 to 3 grams of potato starch or 5 grams soluble starch with 100 c.c. of 1 per cent salicylic acid solution, add 300 to 400 c.c. boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(e) Potassium Iodide Solution

Dissolve 150 grams of potassium iodide free from iodate in distilled water and dilute to 1000 c.c.

(f) Hanus Solution

Dissolve 13.2 grams of iodine in 1000 c.c. of 99.5 per cent glacial acetic acid which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 c.c. of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(g) Alcoholic Sodium Hydroxide Solution

Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 grams per 1000 c.c. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 grams to 1000 c.c.), kept at about 50° C. for 15 days and then distilled.

(h) Uranyl Indicator for Zinc Titration

A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(i) Standard Potassium Ferrocyanide

Dissolve 22 grams of the pure salt in water and dilute to 1000 c.c. To standardize, transfer about 0.2 gram (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400-c.c. beaker. Dissolve in 10 c.c. hydrochloric acid and 20 c.c. water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid, and then add 3 c.c. strong hydrochloric acid. Dilute to about 250 c.c. with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtain when the sample is titrated.

(j) Barium Chloride Solution

Dissolve 100 grams of pure crystallized barium chloride in water and dilute to 1000 c.c.

CHAPTER VI

LITHOPONE[1]

This pigment is a chemically precipitated pigment containing approximately from 69 to 70 per cent barium sulphate, the remainder consisting of zinc sulphide, with occasional impurities of zinc oxide and carbonate.

Analysis

Moisture

Heat 2 grams for two hours at 105° C.

Barium Sulphate

Treat 1 gram with 10 c.c. conc. HCl and 1 gram of potassium chlorate, added in small amounts. Evaporate to one-half its volume, add 100 c.c. hot water and a few c.c. of dilute H_2SO_4. Boil, filter, wash and weigh the insoluble residue, which should show only the presence of barium sulphate. Examine the residue for silica and alumina.

Total Zinc

Determine the total zinc in the filtrate by the volumetric method as outlined under Sublimed White Lead.

[1]Standard Methods of Chemical Analysis, Scott, p. 630.

Zinc Sulphide

Digest 1 gram at room temperature for one-half hour with 100 c.c. of 1 per cent acetic acid. Filter and determine the zinc in the precipitate by solution in HCl as under Sublimed White Lead.

Zinc soluble in acetic acid is reported as zinc oxide, zinc insoluble as zinc sulphide. The filtrate from the acetic acid treatment, after precipitating the zinc as zinc sulphide and subsequent removal, should be examined for barium which might be present as carbonate, and calcium, present as either sulphate or carbonate.

U. S. Interdepartmental Committee's Recommended Laboratory Examination for Flat Interior Lithopone Paint, White and Light Tints[1]

1. Laboratory Examination

(a) Caking in Container

When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paint must be no more difficult to mix to a uniform consistency than a good grade of flat paint. The paint shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the orig-

[1]Prepared and recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization, January 21, 1921. P. H. Walker, Bureau of Standards, Chairman; J. W. Ginder, Treasury Department, Secretary. Circular of the Bureau of Standards. No. 111.

inal package gives the net weight of the contents. A portion of the thoroughly mixed paint shall be placed in a clean container and portions for the remaining tests promptly weighed out.

(b) Color

Place some of the paint on a clean, clear glass plate. Place some of the standard agreed upon beside the sample on the plate, turn the glass over, and compare the colors.

(c) Weight Per Gallon

Weigh a clean, dry 100-c.c. graduated flask. Fill to the mark with the thorougly mixed paint and weigh again. The increase in weight expressed in grams, divided by 100, gives the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon.

(d) Brushing Properties, Time of Drying, and Resistance to Washing

Brush the well mixed paint on a suitable panel which may be ground glass, steel, or well filled wood. Note whether the paint works satisfactorily under the brush. Place the panel in a vertical position in a well-ventilated room and let it stand for 18 hours. The paint should be dry and free from streaks. Let the panel stand for five days, then make marks on it with a soft lead pencil (No. 2, Mogul) and wash these marks off with warm (75° C.) distilled water and white floating soap, using a sponge or soft rag. The marks must be removed by this treatment without appreciably marring the paint film.

(e) Fastness to Light

Apply a sufficient number of coats of the paint to a ground glass plate to completely hide the surface, cover half of this painted surface with opaque black paper, and expose indoors in a well lighted room for five days. Remove the black paper and examine the surface. The exposed portion should be no darker than the portion protected by the black paper.

(f) Water

Mix 100 grams of the paint in a 300-c.c. flask with 75 c.c. of toluol. Connect with a condenser and distill until about 50 c.c. of distillate has been collected in a graduate. The temperature in the flask should be then about 105 to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint. Material complying with the specification should yield less than 1.0 c.c.

(g) Volatile Thinner

Weigh accurately from 3 to 5 grams of the paint into a tared flat bottomed dish about 5 cm. in diameter, spreading the paint over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate the loss in weight as percentage of water and volatile thinner, subtract from this the percentage of water (1 (*f*)), and report the remainder as volatile thinner.

(h) Percentage of Pigment

Weigh accurately about 15 grams of the paint into a weighed centrifuge tube. Add 20 to 30 c.c.

of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 50 c.c. in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 c.c. of extraction mixture and once with 40 c.c. of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment. Grind the pigment to a fine powder, pass through a No. 80 sieve to remove any skins, and preserve in a stoppered bottle. Preserve the extracted vehicle for 1 (*i*).

(i) Percentage of Non-Volatile Vehicle

Add together the percentages of water (1 (*f*)), of volatile thinner (1 (*g*)), and of pigment (1 (*h*)), and subtract the sum from 100. The remainder is the percentage of non-volatile vehicle, which should be not less than one-third as large as the percentage of volatile thinner.

(j) Nature of Non-Volatile Vehicle

Evaporate the extracted vehicle and extraction mixture from 1 (*h*) to about 5 c.c. Thoroughly clean with benzol a piece of bright sheet iron, tin plate, or terneplate. Spread a portion of the con-

centrated extracted vehicle on the sheet of metal, allow to dry for 30 minutes at room temperature in a vertical position, bake for three hours at 100 to 110° C. (212 to 221° F.), remove from the oven, and keep at room temperature for three days. Test the film with a knife blade at a place not less than 2.5 cm. (1 inch) from the edge. The film should be tough and elastic; if it powders or if particles fly under the test, it will be considered brittle, which will be cause for rejection. The film must also stand light, vigorous rubbing with the finger without powdering or disintegrating.

(k) Coarse Particles and "Skins"

Dry in an oven at 105 to 110° C. a No. 200 sieve, cool, and weigh accurately. Weigh an amount of paint containing 30 grams of pigment (see 1 (*h*)), add 50 c.c. of kerosene, mix thoroughly, and wash with kerosene through the sieve, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles too coarse to pass the sieve have been washed through, wash all kerosene from the sieve with ether or petroleum ether, heat the sieve for one hour at 105 to 110° C., cool, and weigh. The total residue left on the sieve should be not more than 0.15 gram.

2. Analysis of Pigment

Use the pigment extracted in 1 (*h*).

(a) Qualitative Analysis

Make qualitative analysis following ordinary methods.

(b) Matter Soluble in Water

Transfer 2.5 grams of the pigment to a graduated 250-c.c. flask, add 100 c.c. of water, boil for five minutes, cool, fill to mark with water, mix, and allow to settle. Pour the supernatant liquid through a dry filter paper and discard the first 20 c.c. Then evaporate 100 c.c. of the clear filtrate to dryness in a weighed dish, heat for one hour at 105 to 110° C., cool, and weigh. The residue should not exceed 0.008 gram.

(c) Barium Sulphate and Siliceous Material

Transfer 1 gram of pigment to a porcelain casserole or dish, moisten with a few drops of alcohol, add 40 c.c. of hydrochloric acid (1.1, specific gravity), cover, and boil to expel hydrogen sulphide; remove the cover and evaporate to dryness on the steam bath, moisten with hydrochloric acid, dilute with water, filter through paper, and wash with dilute hydrochloric acid and then with hot water until the washings are free from zinc and chlorine. Ignite and weigh the residue, which will be barium sulphate and siliceous material.

Mix the ignited residue with about 10 times its weight of anhydrous sodium carbonate (grind the mixture in an agate mortar if necessary), fuse the mixture in a covered platinum crucible, heating about one hour. Let cool, place the crucible and cover in a 250-c.c. beaker, add about 100 c.c. of water, and heat until the melt is disintegrated. Filter on paper (leaving the crucible and cover in the beaker) and wash the beaker and filter thor-

oughly with hot water to remove soluble sulphates. Place the beaker containing the crucible and cover under the funnel, pierce the filter with a glass rod, and wash the carbonate residue into the beaker by means of a jet of hot water. Wash the paper with hot dilute hydrochloric acid (1:1), and then with hot water. If the carbonate residue is not completely dissolved, add sufficient dilute hydrochloric acid to effect solution, and remove the crucible and cover, washing them with a jet of water. Heat the solution to boiling and add 10 to 15 c.c. of dilute sulphuric acid, and continue the boiling for 10 or 15 minutes longer. Let the precipitate settle, filter on a weighed Gooch crucible, wash with hot water, ignite, cool, and weigh as $BaSO_4$. Subtract from the result of the previous determination to obtain the siliceous material.

(d) Total Zinc Calculated as Zinc Oxide

With material containing no interfering elements (iron, for example), weigh accurately about 1 gram of pigment, transfer to a 400-c.c. beaker, moisten with alcohol, add 30 c.c. of hydrochloric acid (1:2), boil for two to three minutes, add 200 c.c. of water and a small piece of litmus paper; add strong ammonia until slightly alkaline, render just acid with hydrochloric acid, then add 3 c.c. of strong hydrochloric acid, heat nearly to boiling, and titrate with standard ferrocyanide as in standardizing that solution (see reagents). Calculate total zinc as zinc oxide.

When iron or other interfering elements are present (see 2 (*a*)), take the filtrate containing the zinc from 2 (*c*), add a slight excess of bromine water and 2 grams ammonium chloride, heat to nearly boiling, add an excess of ammonia, heat for about two minutes, filter, dissolve the precipitate in hydrochloric acid, add 2 grams of ammonium chloride, and reprecipitate with ammonia as above. Filter, wash the precipitate with hot 2 per cent ammonium chloride solution, unite the two filtrates, and determine zinc as above.

(e) Zinc Oxide

Weigh accurately 2.5 grams of pigment, transfer to a 250-c.c. graduated flask, moisten with a few drops of alcohol, add about 200 c.c. of 1 to 3 per cent acetic acid, shake vigorously and let stand for 30 minutes, shaking once every five minutes. Fill to the mark with 1 to 3 per cent acetic acid, mix, filter through a dry paper, discard the first 25 c.c., and determine zinc in 100 c.c. of the filtrate (corresponding to 1 gram) as in 2 (*d*). Calculate the percentage of zinc oxide.

(f) Calculations

Subtract the percentage of zinc oxide (2 (*e*)) from the percentage of total zinc as zinc oxide (2 (*d*)) and multiply the remainder by 1.2 to convert to percentage of zinc sulphide. In case the percentage of barium sulphate (2 (*c*)) is not more than 2.86 times as great as the percentage of zinc sulphide, add the two together and call the sum the

percentage of lithopone. If the percentage of barium sulphate is greater than this amount take 2.86 times the percentage of zinc sulphide as the percentage of barium sulphate to be included in the percentage of lithopone and include the remainder in the percentage of tinting and extending pigments. Subtract the sum of the percentages of zinc oxide (2 (*e*)), lithopone, and matter soluble in water (2 (*b*)) from 100. Call the remainder percentage of tinting and extending pigments.

3. Reagents

(a) Extraction Mixture

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(b) One to Three Per Cent Acetic Acid

Dilute 20 c.c. glacial acetic acid to 1000 c.c. with distilled water.

(c) Uranyl Indicator for Zinc Titration

A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(d) Standard Potassium Ferrocyanide

Dissolve 22 grams of the pure salt in water and dilute to 1000 c.c. To standardize, transfer about 0.2 gram (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400-c.c. beaker. Dissolve in 10 c.c. of hydrochloric acid

and 20 c.c. of water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid, and then 3 c.c. of strong hydrochloric acid. Dilute to about 250 c.c. with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume and acidity as obtain when the sample is titrated.

CHAPTER VII

A COLORIMETRIC METHOD FOR THE DETERMINATION OF COPPER AND IRON IN PIG LEAD, LEAD OXIDES, AND LEAD CARBONATE[1]

Most methods in use for the determination of the small percentage of copper contained in pig lead, lead oxides and lead carbonate are long and tedious. This is especially true in those instances where refined metal serves as the base for the finished product and the copper content being extremely low, many difficulties present themselves; these can be overcome by the use of this colorimetric method.

While the estimation of the iron content in these compounds can be readily carried out colorimetrically by a separate analysis,[2] it has been found that the following method, which combines the determination of both copper and iron colorimetrically in one analysis, adds greatly to the rapidity and accuracy in finding the percentages of these impurities. The method not only eliminates the use of hydrogen sulphide, but it shortens the time of a single analysis to 30 or 40 minutes, while the results attain the same degree of accuracy as those

[1] J. Ind. Eng. Chem., 7, 1035 (1915).
[2] J. Ind. Eng. Chem., 4, 659 (1912).

established by the longer and more complicated methods.

The method of procedure varies somewhat with the nature of the sample to be examined: hence, it will be necessary to make especial mention of red lead.

Analysis of Pig Lead, Litharge and Lead Carbonate for Copper

Weight of Sample

In analyzing refined pig lead, or lead compounds made from refined metals, it is necesary, owing to the small percentages of copper and iron usually present, to use large samples. It has been found, by the use of this method, that smaller samples may be used with equally accurate results, thereby reducing the bulk to be handled and eliminating any errors which frequently result from the use of large volumes. A sample weighing 30 grams has been found sufficiently large for refined products, and not over 10 grams need be used for the crude or unrefined material.

Method of Procedure

Weigh the finely divided sample into a 400-c.c. beaker, and add small portions of hot (1:1) nitric acid until solution is effected. If any basic lead nitrate has been formed, dilute slightly with warm water and boil. Add 32 c.c. (1:1) sulphuric acid, stirring constantly while adding. Let

the precipitate settle, and decant filtrate through a coarse filter paper. Wash four times by decantation, using small portions of warm, distilled water. Transfer the precipitate to the paper, wash again and allow to drain. Make the filtrate neutral with ammonium hydroxide and add 4 c.c. excess. Boil for a short time and filter. Wash the precipitate well with warm water, and reserve for the determination of the iron. Render the filtrate acid with special c. p. hydrochloric acid, adding not more than two drops excess. Add six drops of (1:10) potassium ferrocyanide solution, filter through close filter papers using two to each funnel. Catch the filtrate and inspect for copper ferrocyanide. Let the precipitate drain well without washing. Dissolve the copper ferrocyanide off of the paper with alternate washings of small portions of ammonium hydroxide and hot water. Wash well and keep the bulk to 30 or 40 c.c. Render slightly acid with hydrochloric acid, adding not over two drops excess. Transfer to a 100-c.c. Nessler tube, and dilute to mark with distilled water. The copper is then determined colorimetrically according to a modification of the method of Carnelly.[1]

ERRATUM

Page 61—Last paragraph should read as follows:

In another Nessler tube, place 10 c.c. of 5 per cent ammonium nitrate solution, six drops of (1:10) potassium ferrocyanide solution, two drops concentrated nitric acid and 90 c.c. distilled water, add from a burette graduated to tenths of 1 c.c., standard copper sulphate solution until the color matches the sample under examination.

Standard Copper Sulphate Solution[1]

"Dissolve 0.393 gram of pure $CuSO_4.5H_2O$, in one liter of distilled water. 1 c.c. = 0.0001 gram of copper," or 0.00033 per cent when using a 30 gram sample.

Analysis of Red Lead for Copper

Treat 30 grams of the sample with 40 c.c. (1:1) nitric acid, using great care that the violence of the reaction does not cause the sample to froth over the beaker. Slowly add 30 to 40 c.c. of 3 per cent hydrogen peroxide, stirring constantly. Boil until solution is effected, and proceed as directed under the "Analysis of Pig Lead," on page 60.

Sodium sulphite c. p. may be used in place of the hydrogen peroxide for effecting the solution of lead peroxide, adding it dry in small portions and boiling until no brown lead peroxide is present.

Determination of Iron in the Above Compounds

For the iron determination, use the precipitate of iron hydroxide removed from the copper solution, proceeding as follows: Dissolve the precipitate contained on the paper with (1:1) hydrochloric acid, collecting the filtrate in a 300-c.c. volumetric flask. Wash the paper free from acid with hot, distilled water, dilute to mark, and mix thoroughly.

[1]Sutton's Volumetric Analysis, p. 205.

Place 10 c.c. in a 100-c.c. Nessler tube, add three drops nitric acid, 10 c.c. (1:15) ammonium sulphocyanide solution, dilute to mark and compare with a standard iron solution according to the method outlined by Schaeffer:[1]

"The color is compared with a blank made in the following manner: A solution of ferric ammonium sulphate of known strength is required. This is made by dissolving 0.7022 gram of ferrous ammonium sulphate in water. Acidify with sulphuric acid, heat to boiling and add a solution of potassium permanganate until all the iron is converted to the ferric condition. Only the very slightest pink tinge may be present after the addition of the potassium permanganate, as this tinge will fade away, while the presence of a pink color tends to vitiate the results. Allow the solution to cool and dilute to one liter. One c.c. of this solution equals 0.0001 gram of iron.

Prepare the blank by pouring into a 100-c.c. Nessler cylinder, 10 c.c. ammonium sulphocyanide solution, and three drops of concentrated nitric acid. Dilute to 100 c.c. and titrate to the exact color developed in the sample under examination, by the addition of the standard ferric ammonium sulphate solution. One c.c. of this solution equals 0.01 per cent iron as the 10 c.c. removed from the flask contained 1 gram sample. It will be found that the color can be accurately compared to within 0.001 per cent of iron content."

[1] J. Ind. & Eng. Chem., 4 (1912), 659.

Comparison of Results on Copper

Table I shows the results obtained by the above method, as compared with the method set forth by Fresenius,[1] on two sets of samples and a copper sulphate solution of known strength.

TABLE I—COMPARATIVE RESULTS (PERCENTAGES CU) BY METHOD OF FRESENIUS AND OF AUTHOR.

	Pig Lead		Litharge and Red Lead		$CuSO_4$ Solution		
No.	Fres.	Color.	Fres.	Color.	Fres.	Color.	% Cu present
1.....	0.0009	0.00088	0.002	0.002	0.002	0.002	0.002
2.....	0.0013	0.0013	0.0008	0.0008	0.0008	0.0008	0.0008
3.....	0.0009	0.00088	0.0009	0.00088	0.00066	0.00066	0.0007
4.....	0.002	0.002	0.0007	0.0007	0.001	0.001	0.001
5.....	0.001	0.001	0.0015	0.0015	0.00066	0.00066	0.00066
6.....	0.0015	0.0015	0.0038	0.0038	0.0015	0.0015	0.0015
7.....	0.0012	0.0012	0.00088	0.00088	0.00088	0.00088	0.00088
8.....	0.0079	0.0079	0.00088	0.0009	0.0009	0.00088	0.0009
9.....	0.0013	0.0013	0.0013	0.0013	0.0015	0.0015	0.0015
10.....	0.0004	0.0004	0.00066	0.00066	0.0007	0.00066	0.0007

Precautions and Interfering Elements

If the sample contains much zinc, the following method may be used for removing it: The filtrate from the iron precipitation, before precipitating the copper ferrocyanide, is rendered slightly acid with acetic acid, and 5 c.c. of an 8 per cent sodium ammonium phosphate solution are added; boil, cool, filter and treat the filtrate as before outlined.

Lead, when present in not too large quantity, has little or no effect on the accuracy of the colorimetric comparison of copper. If a faint white cloud of lead ferrocyanide should develop in the sample under examination, the addition of a small amount of very dilute lead nitrate solution to the standard will overcome this difficulty.

[1] Fresenius' Quantitative Chemical Analysis, Vol. II, p. 584.

Reagents and Indicators

This method presupposes the use of absolutely pure reagents, especially free from iron and copper . Use litmus paper as an indicator, as all other indicators, once introduced, will affect the final color.

CHAPTER VIII

RED LEAD AND ORANGE MINERAL

These two compounds are oxides of lead, of an approximate formula, Pb_3O_4, being probably a combination of lead dioxide and lead monoxide. They are found on the market as milled oxides and flake oxides. In some instances oxides are found which are artificially colored with organic dyes.

Analysis

The analysis of red lead and orange mineral consists in the determination of the red lead content or the lead dioxide content, moisture, iron, silica, copper and metallic lead. It is also necessary to determine from a physical standpoint the apparent gravity or density, which may be done by determining the weight of a cubic inch of the material, as outlined on page 148.

Moisture

Dry 2 grams of the sample for 2 hours at 105° C. The loss will be moisture.

Red Lead, or Lead Dioxide[1]

Treat 1 gram of the sample in a beaker with 15 c.c. of nitric acid, specific gravity 1.2 (110 c.c. nitric acid, specific gravity 1.42, to 100 c.c. of water. This solution should be aerated to free it from all nitrous fumes).

[1]J. Ind. Eng. Chem., 8, 237 (1916).

Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 c.c. of dilute hydrogen peroxide (1 part of 3 per cent hydrogen peroxide to 3.5 parts of water). Add about 50 c.c. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely passed into solution, dilute with hot water to about 250 c.c. volume and titrate directly with a standard potassium permanganate solution, having an iron value of 0.005. Titrate to the faint pink permanganate color. A blank titration on the hydrogen peroxide solution must now be made.

Titration of Hydrogen Peroxide, and Calculation of Results

Into a beaker pour 15 c.c. of nitric acid having the strength as above given and add exactly the same amount of hydrogen peroxide (10 c.c.). Dilute to 250 c.c. with hot water and titrate with standard potassium permanganate to a faint pink color.

The difference between the number of cubic centimeters of potassium permanganate required for the blank titration and the number required for the red lead titration is the amount of potassium permanganate required for the hydrogen peroxide which was reacted on by the lead dioxide. The difference between the two amounts of potassium

permanganate required multiplied by 3.058 gives the percentage of red lead present according to the following proportion:

Let X = % Pb_3O_4 per c.c. difference
2 Fe : Pb_3O_4 :: 0.005 : X
112 : 685 :: 0.005 : X
X equals 3.058

To determine the lead dioxide present multiply this difference by 1.067 according to the following proportion:

Let Y = % PbO_2 per c.c. difference
2 Fe : PbO_2 :: 0.005 : Y
112 : 239 :: 0.005 : Y
Y equals 1.067

These calculations have been arranged in a series so devised as to permit the direct reading of the red lead percentage. The basis of the calculations depends on the fact that each c.c. of potassium permanganate solution (iron value, 0.005) is equivalent to 3.058 per cent of true red lead; or, each 0.1 c.c. is equivalent to 0.3058 per cent true red lead on a one gram sample.

A red lead or orange mineral having 100 per cent true red lead content requires 32.7 c.c. potassium permanganate solution of the above strength.

The calculation, therefore, arranges itself as follows: Each 0.1 c.c. on the selected burette represents 0.3058 per cent true red lead. The number 32.7 being equivalent to 100 per cent occupies an analogous position on the chart. A representative

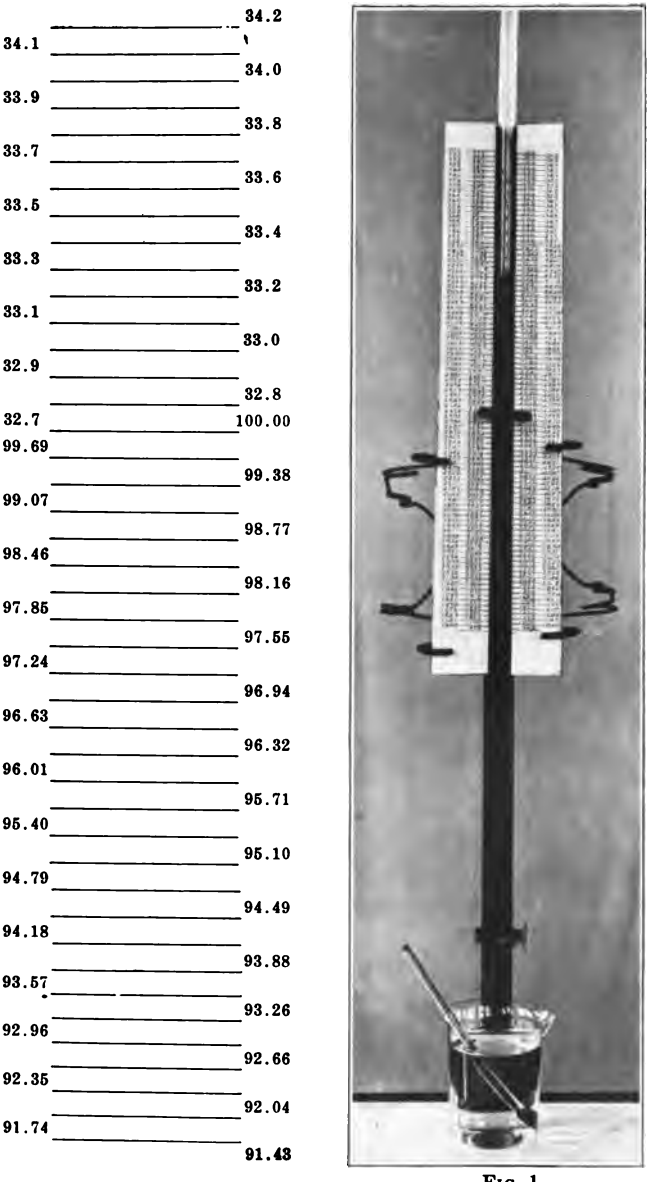
34.2
34.1
34.0
33.9
33.8
33.7
33.6
33.5
33.4
33.3
33.2
33.1
33.0
32.9
32.8
32.7
100.00
99.69
99.38
99.07
98.77
98.46
98.16
97.85
97.55
97.24
96.94
96.63
96.32
96.01
95.71
95.40
95.10
94.79
94.49
94.18
93.88
93.57
93.26
92.96
92.66
92.35
92.04
91.74
91.43

FIG. 1

portion of the series is shown alongside of figure one. The series continues upward in steps of 0.1 and downward in steps of 0.30 and 0.31 to such points as are required for the red lead usually examined.

Fig. 1 is an illustration of the apparatus in use; calculations should be continued upward to 40.0 or to that point where the hydrogen peroxide solution used is of such strength that 10 c.c. of the hydrogen peroxide solution require 40 c.c. of the potassium permanganate solution. Calculations should be continued downward to 9.48 per cent true red lead content.

In using the series the chart is attached to the burette by a screw clamp. The blank determination is first made on the hydrogen peroxide solution and the value found is placed opposite zero on the burette. In the analysis of the red lead the value is then read off directly. As a hypothetical case we will use a hydrogen peroxide solution with a blank titration of 34.1 c.c. In the analysis of a red lead or orange mineral 4.2 c.c. of the potassium permanganate solution is required for a final titration value. The calculation shows the difference between the two readings to be 29.9 c.c. or multiplied by 3.058 equals a true red lead percentage of 91.43 per cent. Comparing this with the series of calculations we find 4.2 c.c. from the 34.1 to be 91.43 per cent.

Should it be preferred to determine the lead peroxide content, the calculation will be based on

the value 0.1067 for each 0.1 c.c. of the potassium permanganate solution. It is understood that the division must be made to correspond to the 0.1 c.c. divisions on the burette.

It is always advisable to make several blank determinations each day where this analysis is constantly made and when only occasionally used a blank titration should be made before each analysis.

The strength of the hydrogen peroxide solution will vary but the permanance of the permanganate solution renders the method accurate over a long period of time.

ERRATUM

Page 71—Heading, "Standard Potassium Permanganate," Line 4—For "5.75 *grains* c. p. salt" read "5.75 *grams* c. p. salt."

place for a week or more. By this time all organic matter will have been oxidized and after filtering the solution through an asbestos filter the solution is ready for standardization. As small amounts of MnO_2 destroy the permanence of this solution, it is necessary that it be removed by filtering. The method described in Bureau of Standards Circular No. 40 should be used. This method is as follows:

In a 400-c.c. beaker, 0.25 gram of sodium oxalate is dissolved in 200 to 225 c.c. of hot water (80-90° C.) and 10 c.c. of (1:1) sulphuric acid added. The solution is at once titrated with the solution of permanganate, the solution being stirred continuously

and vigorously. The permanganate must be added at the rate of 10 to 15 c.c. per minute and the last 0.5 to 1 c.c. must be added drop by drop, each drop being allowed to decolorize fully before the next is added. The solution should not be below 60° C. by the time the titration is completed. With a permanganate solution having an iron value of 0.005 per c.c., 41.66 c.c. of the permanganate are required to react with 0.25 gram sodium oxalate.

If the first titration shows that the solution is too strong a small amount of distilled water should be added. To calculate exactly how much water to add divide 41.66 by the number c.c. required in the titration and multiply by the number of c.c. remaining in the bottle. The difference between this product and the number of c.c. in the bottle will be the volume of water to add.

If the solution is too weak this difference multiplied by 0.00283 will be the grams of potassium permanganate salt to add. After the addition of water or salt the solution should again be titrated and if a titer of 41.66 is not obtained water or salt added until this titer is obtained. A solution carefully prepared in this manner should keep for months.

Flake Red Lead

In certain instances it is found that flake red lead is soluble only with the greatest difficulty by the above procedure. In cases where this difficulty is encountered the following method will be found to give excellent results:

Digest 1 gram of the sample in a beaker with 15 c.c. of nitric acid made up of a strength as given in the previous method. Boil the solution for a short time, add 10 c.c of a standard oxalic acid solution, the strength of which has been previously determined. Add 2 c.c. of sulphuric acid (1:1). Boil the solution and titrate with a standard solution of potassium permanganate having an iron value of 0.005. A blank titration on the same amount of oxalic acid must be made. The difference between the amount of potassium permanganate required for the blank titration and that required for the red lead titration multiplied by the factor 3.058 or 1.067 will give the content of red lead or lead dioxide according to the proportions in the previous analysis.

Iron

The iron should be determined colorimetrically as described on page 62.

Copper

This constituent may be determined gravimetrically, or colorimetrically.

By the gravimetric method twenty grams of the sample are treated in a large beaker with 50 c.c. of nitric acid, 25 c.c. of water and sufficient hydrogen peroxide to cause complete solution of the lead dioxide.

Determine the copper as outlined under the Analysis of Litharge.

The colorimetric method described on page 62, however, is more rapid and convenient.

Silica

Silica is found to be present in oxides of lead both as free silica and as lead silicate, though usually in inappreciable amounts.

Digest 2 grams of the sample in a casserole with 2 grams of potassium chlorate and 15 c.c. of dilute nitric acid. Proceed from this point as outlined under the Analysis of Litharge, page 88.

Organic Color

The adulteration of red lead and orange mineral with organic coloring matter may be detected by adding 20 c.c. of 95 per cent alcohol to 2 grams of the oxide, heating to boiling and allowing to settle. Pour off the supernatant liquid, boil with water, allow to settle and add a very small amount of ammonium hydroxide. If either the alcohol, water or ammonium hydroxide are colored, it indicates organic coloring matter. The quantitative determination is exceedingly difficult and the organic color is usually estimated by difference.

U. S. Interdepartmental Committee's Recommended Laboratory Examination for Red Lead, Dry and Paste[1]

1. Laboratory Examination, Dry Pigment

(a) Qualitative Analysis

Follow ordinary methods of qualitative analysis. The material should give a negative test for matter

[1]Prepared and recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization, January 26, 1920. P. H. Walker, Bureau of Standards, Chairman; H. E. Smith, U. S. Railroad Administration, Secretary. Circular of the Bureau of Standards. No. 90.

insoluble in a mixture of nitric acid and hydrogen peroxide, and material other than oxides of lead. (If more than a faint cloud remains after treatment with nitric acid and hydrogen peroxide, it will be necessary to take a weighed sample and determine the percentage of this insoluble matter.) Boil 2 grams of the sample with 25 c.c. of 95 per cent ethyl alcohol, let settle, decant off the supernatant liquid, boil the residue with water, decant as before, and boil the residue with very dilute ammonia. If the alcohol, water, or ammonia are colored, organic coloring matter is indicated, which is cause for rejection.

(b) True Red Lead

Weigh accurately 1 gram of the sample into a 200-c.c. Erlenmeyer flask, add a few drops of distilled water, and rub the mixture to a smooth paste with a glass rod flattened on the end. Mix in a small beaker 30 grams of pure crystallized sodium acetate, 2.4 grams of pure potassium iodide, 10 c.c. of water, and 10 c.c. of 50 per cent acetic acid. Stir until all is liquid, warm gently, and, if necessary, add 2 to 3 c.c. more water. Cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved, add 30 c.c. of water containing 5 to 6 grams of sodium acetate, and titrate at once with standard sodium thiosulphate solution, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yel-

low, rub any undissolved particles up with the rod until free iodine no longer forms, wash off the rod, and add the sodium thiosulphate solution until pale yellow. Add starch solution and titrate until colorless, add standard iodine solution until the blue color is just restored. From the amount of standard iodine solution used, calculate the correction to be applied to the thiosulphate reading, and calculate true red lead (iodine value of thiosulphate $\times$ 2.7 = Pb_3O_4 value).

(c) Water Soluble Matter

Digest 10 grams of the sample with 200 c.c. of hot water on a steam bath for 1 hour; filter and wash with hot water until no residue is left on evaporating a few drops of the washings. Evaporate the filtrate to dryness in a weighed dish on a steam bath, heat for 30 minutes at 105 to 110° C., cool, and weigh.

(d) Coarse Particles

Dry a standard No. 200 brass or copper sieve in an oven at 105 to 110° C., cool, and weigh accurately. Weigh 50 grams of pigment which has been previously thoroughly dried by heating in an oven at 105 to 110° C. until all moisture has been driven off. Transfer to a wide mouth bottle or cylinder of about 300 c.c. capacity, add about 200 c.c. of dry kerosene, stopper, and shake vigorously for about five minutes. Remove the stopper and, with a jet of kerosene, wash back into the cylinder any pigment adhering to the stopper. Pour about 50 c.c. of the kerosene with suspended pig-

ment onto the sieve, let drain through, and gradually transfer the whole of the kerosene and pigment to the sieve, finally using a jet of kerosene to transfer the last of the pigment. With proper manipulation a large portion of the pigment will pass through the sieve during the process of transferring from the cylinder. When all pigment has been thrown on the sieve, wash with a jet of kerosene until no more pigment passes through. To make sure that all particles have been thoroughly washed through, move the sieve from over the vessel, in which the main portion of kerosene and pigment has been caught, to over a clean glass dish resting on a white surface and wash all portions of the sieve with a jet of kerosene, using not less than 200 c.c. of kerosene. This kerosene caught in this dish should be entirely free from pigment. If any pigment can be seen in the liquid, repeat the washing until at least 200 c.c. can be washed through without showing any pigment. Then wash with a jet of kerosene all pigment adhering to the frame of the sieve beneath the wire mesh. Finally, wash the kerosene from the sieve with petroleum ether, dry the sieve at 105 to 110° C., cool, and weigh. The increase in weight should be not more than 0.150 gram.

(e) Running, Streaking, or Sagging

Mix paint and apply as per specifications. About the smallest amount that can be conveniently made up will be 154 grams dry red lead, 40 c.c. raw linseed oil, and 4 c.c. each of turpentine and liquid drier.

2. Laboratory Examination, Paste

(a) Caking in Container

When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of red lead paste. The paste shall finally be thoroughly mixed, removed from the container, the container wiped clean, and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(b) Mixing with Linseed Oil, Running, Streaking, and Sagging

Mix as per specification to a paint, first using only the linseed oil and noting whether the paste breaks up readily and the resulting mixture is smooth. About the smallest amount that can be conveniently made up will be 154 grams red lead paste, 36 c.c. raw linseed oil, and 4 c.c. each of turpentine and liquid drier.

(c) Moisture and Other Volatile Matter

Weigh accurately from 3 to 5 grams of the paste into a tared flat bottomed dish, about 5 cm. in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate the loss in weight as percentage of moisture and other volatile matter.

(d) Percentage of Pigment

Weigh accurately about 15 grams of the paste into a weighed centrifuge tube. Add 20 to 30 c.c. of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture and add sufficient of the reagent to make a total of 60 c.c. in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until clear. Decant the clear supernatant liquid. Repeat the extraction twice with 40 c.c. of extraction mixture, and once with 40 c.c. of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for 2 hours. Cool, weigh, and calculate percentage of pigment.

(e) Examination of Pigment

Grind the pigment from 2 (*d*) to a fine powder, pass through a No. 80 sieve to remove any "skins," preserve in a stoppered tube, and apply tests 1 (*a*), 1 (*b*), and 1 (*c*).

(f) Preparation of Fatty Acids

To about 25 grams of the paste in a porcelain casserole, add 15 c.c. of aqueous sodium hydroxide (see reagents), and 75 c.c. of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 c.c. of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 c.c. will usually suffice),

boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and lead sulphate precipitate, wash once with water; then add 50 c.c. water and 50 c.c. ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 c.c. portion of water and then with 5 c.c. portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask, add 25 to 50 grams of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100-c.c. Erlenmeyer flask. Pass a rapid current of dry air (pass through $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off. The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

Note.—It is important to follow all of the details, since ether generally contains alcohol, and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

(g) Test for Mineral Oil

Place 10 drops of the fatty acid (*f*) in a 50-c.c. test tube, add 5 c.c. of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 c.c. of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(h) Iodine Number of Fatty Acids

Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 gram (0.10 to 0.20 gram) to a 500-c.c. bottle having a well ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 c.c. of chloroform. Whirl the bottle to dissolve the sample. Add 10 c.c. of chloroform to two empty bottles like that used for sample. Add to each bottle 25 c.c. of the Hanus solution (see reagents) and let stand with occasional shaking for one-half hour. Add 10 c.c. of the 15 per cent potassium iodide solution and 100 c.c. of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 c.c. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to

1 gram of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(i) Coarse Particles and "Skins"

Weigh an amount of paste containing 50 grams of pigment (see 2 (*d*)), add 200 c.c. of kerosene, and wash through a No. 200 sieve as in 1 (*d*). The residue remaining in the sieve shall not be more than 0.25 gram.

3. Reagents

(a) Extraction Mixture

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(b) Aqueous Sodium Hydroxide

Dissolve 100 grams of sodium hydroxide in distilled water and dilute to 300 c.c.

(c) Standard Sodium Thiosulphate Solution

Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 grams of crystallized sodium thiosulphate to 1000 c.c. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, Vol. II, 3d ed., p. 646.) This solution will be approximately decinormal and it is best to leave it as it is after determining its exact iodine value, rather than to

attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(d) Starch Solution

Stir up 2 to 3 grams of potato starch or 5 grams of soluble starch with 100 c.c. of 1 per cent salicylic acid solution, add 300 to 400 c.c. of boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(e) Standard Iodine Solution

Dissolve 13 grams of resublimed iodine and 18 grams of pure potassium iodide (free from iodates) in 50 c.c. of distilled water, and dilute to 1000 c.c. Determine its exact value by titrating with the standard sodium thiosulphate solution.

(f) Potassium Iodide Solution

Dissolve 150 grams of potassium iodide, free from iodate, in distilled water and dilute to 1000 c.c.

(g) Hanus Solution

Dissolve 13.2 grams of iodine in 1000 c.c. of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 c.c. of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(h) Alcoholic Sodium Hydroxide Solution

Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 grams per 1000 c.c. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 grams to 1000 c.c.), kept at about 50° C. for 15 days, and then distilled.

CHAPTER IX

LITHARGE

Litharge, the monoxide of lead, PbO, may contain small percentages of iron, copper, silica, silver and free metallic lead. When the litharge has been made by a process where steam is used, there may be an appreciable amount of moisture present. It appears on the market in two colors, yellow and red. In some instances litharge is found containing a comparatively large percentage of red lead, which in certain uses is undesirable. The determination of each of the foreign constituents in litharge depends largely upon the use to which the litharge is to be put, as in very few cases are all the constituents determined.

Analysis

Moisture

Dry 2 grams of the sample at 105° C. for two hours. The loss will be moisture.

Free Metallic Lead

Two grams of the sample are treated in a beaker with hot water and just sufficient acetic acid is slowly added, to dissolve the lead oxide. Stir the solution well and note whether any lead silicate remains undissolved. Should such remain, continue stirring until solution has been effected. The

solution should never have greater than a 5 per cent acetic acid strength.

Filter the solution and wash the residual metal three or four times by decantation with hot water, having all the wash water pass through the filter paper, which is finally thoroughly washed with hot water. Transfer any metal on the filter paper to the beaker containing the residual lead, add 1 c.c. of concentrated nitric acid and heat to solution. Dilute with 50 c.c. of water, add 1 gram of sodium acetate and follow this with an excess of saturated neutral potassium bichromate solution, sufficient to precipitate all the lead. Boil, dilute to 100 c.c., allow to cool, filter off the lead chromate, wash thoroughly and determine the lead chromate gravimetrically by drying at 100° C. or volumetrically by titration of the chromic acid present as outlined under the Analysis of Lead Ores. The factor for the direct determination of lead is, however, in this case 0.5, as a 2 gram sample is used.

Red Lead

Determine the percentage of red lead present as outlined under the Analysis of Red Lead.

Iron

Treat 1 gram of the sample with 10 c.c. of water and just sufficient nitric acid, added drop by drop, to cause complete solution. Heat to boiling to oxidize all the iron and determine it colorimetrically as outlined on page 62.

Copper

Copper may be rapidly and accurately determined by the method described on page 60. The following gravimetric method, however, may be found more convenient if only a few determinations are to be made.

Twenty grams of the litharge contained in a 200-c.c. flask are dissolved in nitric acid (50 c.c. concentrated nitric acid to 100 c.c. water). Boil to complete solution. Add 40 c.c. of dilute sulphuric acid (1:1), boil gently for one hour and allow to cool. Filter off the lead sulphate and wash the precipitate thoroughly. Nearly neutralize all the free acid present with ammonium hydroxide, render slightly acid with hydrochloric acid, warm the solution and pass in hydrogen sulphide until no further precipitation of sulphide occurs. Filter off the precipitate without washing, using some of the filtrate to transfer the last traces of sulphide to the filter paper. Dissolve the precipitate in a little nitric acid and wash the filter paper thoroughly with hot water. Add 3 c.c. of concentrated sulphuric acid, evaporate until the white fumes of sulphuric acid are evolved and allow the solution to cool. Add a little water and allow to stand for some hours. Filter off the lead sulphate, washing with hot water containing a little sulphuric acid.

Heat the filtrate to boiling and precipitate the copper as sulphide with hydrogen sulphide in an ammoniacal solution. Filter off the copper sulphide through an ashless filter paper, wash, ignite and

weigh in a covered porcelain crucible, from which the heat and cover are occasionally removed for a few seconds.

The precipitate will consist of a mixture of CuO and Cu_2S. Since the percentage of copper is the same in both of these, the copper may be determined by multiplying the amount found by the factor 0.7988.

Silica

Digest 5 grams of the sample in a covered casserole with 2 grams of potassium chlorate and 15 c.c. of dilute nitric acid (1:1). Evaporate to dryness and dehydrate. Treat the residue, after cooling, with hot water and nitric acid. Heat to boiling, and filter the solution through an ashless filter paper. Wash the residue and filter paper thoroughly with hot acid ammonium acetate solution, made up to a strength as outlined under the Analysis of Lead Ores. Should the residue show a trace of iron, wash it thoroughly with dilute hydrochloric acid. Complete the washing with hot water, dry, ignite and weigh as SiO_2. The residue may be volatilized with hydrofluoric acid, if there is any doubt regarding the purity of the silica.

The silica is present as lead silicate and free silica. The above method determines the total content of silica. The free silica may be determined by dissolving the litharge in dilute nitric acid. Heat to boiling, filter, wash, ignite and weigh as silica.

CHAPTER X

BASIC CARBONATE OF LEAD
(Corroded White Lead)

Basic carbonate white lead ($2PbCO_3.Pb(OH)_2$) contains approximately 80 per cent metallic lead and 20 per cent carbonic acid and combined water, with traces of silver, antimony, lead, and other metals. The analysis of basic carbonate white lead can best be carried out by Walker's method.[1]

Analysis

Total Lead

"Weigh 1 gram of the sample, moisten with water, dissolve in acetic acid, filter, wash, ignite, and weigh the insoluble impurities. To the filtrate from the insoluble matter add 25 c.c. of sulphuric acid (1:1), evaporate and heat until the acetic acid is driven off; cool, dilute to 200 c.c. with water, add 20 c.c. of ethyl alcohol, allow to stand for two hours, filter on a Gooch crucible, wash with 1 per cent sulphuric acid, ignite, and weigh as lead sulphate. Calculate to total lead ($PbSO_4 \times 0.68292 = Pb$) or calculate to basic carbonate of lead (white lead) by multiplying the weight of lead sulphate by 0.85258.

"The filtrate from the lead sulphate may be used to test for other metals, though white lead is only rarely adulterated with soluble substances; test,

[1] P. H. Walker, Bureau of Chemistry Bulletin No. 109, revised, U. S. Dept. of Agriculture, pp. 21 and 22.

however, for zinc, which may be present as zinc oxide.

"Instead of determining the total lead as sulphate it may be determined as lead chromate by precipitating the hot acetic acid solution with potassium bichromate, filtering on a Gooch crucible, igniting at a low temperature, and weighing as lead chromate.

Complete Analysis

"When it is necessary to determine the exact composition of a pure white lead, heat 1 gram of the pigment in a porcelain boat in a current of dry, carbon dioxide free air, catching the water in sulphuric acid and calcium chloride and the carbon dioxide in soda lime or potassium hydroxide (1.27 specific gravity). By weighing the residue of lead monoxide in the boat all the factors for determining the total composition are obtained. Figure the carbon dioxide to lead carbonate ($PbCO_3$), calculate the lead monoxide corresponding to the lead carbonate ($PbCO_3$) and subtract from the total lead monoxide, calculate the remaining lead monoxide to lead hydroxide ($Pb(OH)_2$), calculate the water corresponding to lead hydroxide and subtract from the total water, the remainder being figured as moisture.

"This method assumes the absence of acetic acid. Thompson[1] states that acetic acid varies from 0.05 per cent in Dutch process white lead to 0.7 per cent in some precipitated white leads. It is then more accurate to determine the carbon dioxide by evolu-

[1] J. Soc. Chem. Ind., 1905, 24:487.

tion; this is especially the case when working with a lead extracted from an oil paste, as the lead soap and unextracted oil will cause a considerable error by the ignition method. In determining carbon dioxide by the evolution method, liberate the carbon dioxide with dilute nitric acid, have a reflux condenser next to the evolution flask and dry the carbon dioxide with calcium chloride before absorbing it in the potassium hydroxide bulbs.

Acetic Acid

"It is sometimes necessary to determine acetic acid. Thompson's method[1] is as follows:

"Eighteen grams of the dry white lead are placed in a 500-c.c. flask, this flask being arranged for connection with a steam supply and also with an ordinary Liebig condenser. To this white lead is added 40 c.c. of syrupy phosphoric acid, 18 grams of zinc dust, and about 50 c.c. of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same small bulk—this operation being conducted twice. The distillate is then transferred to a special flask and 1 c.c. of syrupy phosphoric acid added to insure a slightly acid condition. The flask is then heated and distilled down to a small bulk—say, 20 c.c. Steam is then passed through the flask until it contains about 200

[1] J. Soc. Chem. Ind., 1905, 24:487.

c.c. of condensed water, when the steam is shut off and the flask heated directly. These operations of direct distillation and steam distillation are conducted until 10 c.c. of the distillate require but a drop of tenth normal alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with tenth normal sodium hydroxide, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to 600-700 c.c., to titrate the distillate when it reaches 200 c.c., and so continue titrating every 200 c.c. as it distills over.

"If the white lead contains appreciable amounts of chlorine it is well to add some silver phosphate to the second distillation flask and not carry the distillation from this flask too far at any time.

"The method used by the chemists of the Navy Department is as follows: Weigh 25 grams of white lead in an Erlenmeyer flask, add 75 c.c. of 25 per cent phosphoric acid, distill with steam to a 500 c.c. distillate, add to the distillate some milk of barium carbonate, bring to a boil, filter, keeping the solution at the boiling point (it is not necessary to wash), add an excess of sulphuric acid to the filtrate and determine the barium sulphate in the usual manner; subtract 53 milligrams from the weight of the barium sulphate and calculate the remainder as acetic acid ($BaSO_4$ times 0.515 equals CH_3COOH). The object of this rather indirect method is to avoid any error that might arise from fatty acids being carried over by the steam distilla-

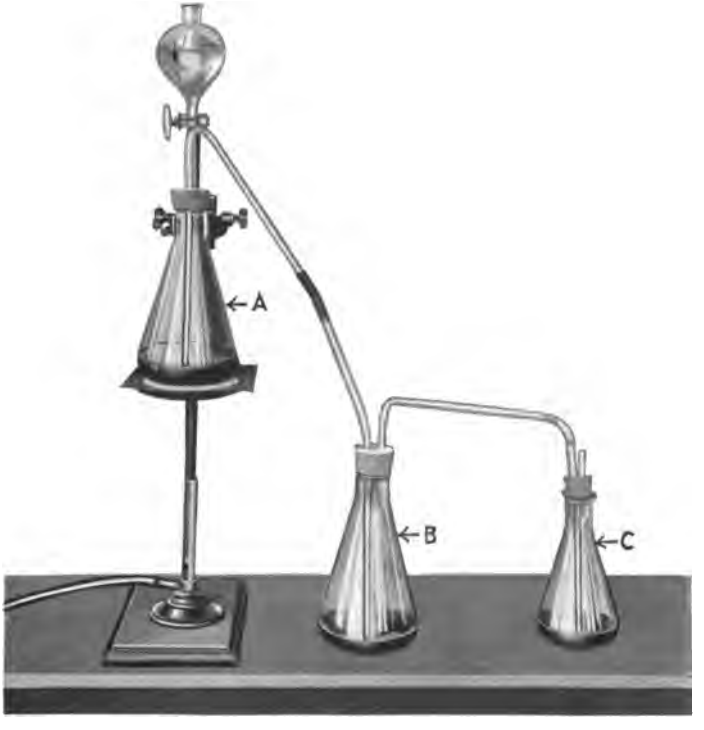

FIG. 2. Carbon Dioxide Apparatus.

tion. For white lead that has not been ground in oil, Thompson's method is to be preferred."

Carbonic Acid

The carbonic acid content of white lead may be determined by using the Scheibler apparatus, complete reference to which, with all tables, may be found in "The Analysis of Paints and Painting Materials,"[1] page 6. A more simple and efficacious method of determining the carbonic acid content will be found in the following method.

The method can be used in such cases where the substances to be analyzed evolve gases other than carbon dioxide; that is, hydrogen sulphide, sulphur dioxide, or organic matter. The apparatus used is shown in Fig. 2. A weighed sample of the substance is introduced into the Erlenmeyer flask (A). Into flask (B) is placed a 10 per cent solution of barium chloride, more than sufficient to hold the carbon dioxide evolved, and 20 c.c. of concentrated ammonium hydroxide free from carbon dioxide. If sulphides are present, it is sometimes advisable to pass the liberated gas first through a few c.c. of strong potassium permanganate. The flask (B) is warmed until completely filled with ammonia fumes. Flask (D) is a safety bottle containing the same solution as flask (B). Only in rare cases will any trace of the carbon dioxide be noticed in the safety flask. After flask (B) is completely filled with ammonia vapor,

[1] The Analysis of Paints and Painting Materials, Gardner and Schaeffer: The McGraw-Hill Book Company, New York.

make all connections and allow the hydrochloric acid to drop slowly from the separatory funnel into the decomposition flask (A). When effervescence has ceased, heat the contents of the flask until filled with steam. The delivery tubes and sides of the precipitating flask are then washed with boiling water, the flask is filled to the neck, stoppered, and the precipitated barium carbonate allowed to settle. Wash thoroughly by decantation, each time stoppering the flask to prevent any error from the carbon dioxide present in the air, and determine either gravimetrically, by conversion into barium sulphate, or volumetrically, by dissolving in standard hydrochloric acid and titrating the excess of acid used with standard potassium hydroxide. Calculate the barium found to carbonate and the amount of carbon dioxide from the found carbonate. The entire operation may be hastened by conducting a brisk current of air free from carbon dioxide through the entire apparatus.

Two rapid volumetric methods for the determination of carbonic acid contents are described in detail by Leon T. Bonser in the Journal of Industrial and Chemical Engineering, March, 1912, page 203, and by H. W. Brubaker in the same journal, August, 1912.

A few typical analyses of basic carbonate white lead, for impurities, are given in the table on the following page.

TYPICAL ANALYSES OF BASIC CARBONATE WHITE LEAD FOR IMPURITIES.

Insoluble	0.0252	0.0130	0.0241	0.0417	0.0089	0.0307	0.0123	0.0504
Antimony	0.0019	0.0685	0.0035	0.0028	0.0031	0.0074	0.0054	0.0080
Arsenic	0.0001	0.0072	0.0010	0.0024	0.0022	0.0027	0.0018	0.0008
Bismuth	0.0197	0.0165	0.0122	0.0269	0.0329	0.0226	0.0395	0.0133
Silver	none	none	none	none	none	none	none	none
Cadmium	none	none	none	none	none	none	none	none
Copper	0.0005	trace	0.0014	0.0012	0.0013	0.0008	0.0006	0.0111
Nickel	none	trace	trace	none	none	none	trace	none
Zinc	0.0068	0.0005	0.0006	0.0008	0.0009	0.0003	0.0005	0.0003
Manganese	none	none	none	none	none	none	none	none
Calcium	0.0360	0.0057	0.0142	0.0071	0.0143	0.0143	0.0100	0.0172
Iron oxide	0.0038	0.0045	0.0042	0.0035	0.0043	0.0031	0.0035	0.0056
Aluminum oxide	0.0009	0.0005	0.0004	0.0014	0.0001	0.001	0.0049	0.0032
Sulphur trioxide	0.0338	0.0021	0.0105	0.0049	0.0442	0.0049	0.0099	0.0190
Chlorine	0.0299	0.0497	0.0165	0.0403	0.0149	0.0120	0.0125	0.0118
Acetic acid	0.4539	0.3157	0.3060	0.2558	0.2558	0.5462	0.5853	0.2081

U. S. Interdepartmental Committee's Recommended Specification for Basic Carbonate White Lead, Dry and Paste[1]

1. General

Basic carbonate white lead may be ordered in the form of dry pigment or paste ground in linseed oil. Material shall be purchased by net weight.

(a) Dry Pigment

The pigment shall be the product made from metallic lead and shall have a composition corresponding approximately to the formula $2PbCO_3.Pb(OH)_2$. It shall be thoroughly washed after corroding, shall be free from impurities and adulterants, and shall meet the following requirements:

Color — Color Strength

When specified, shall be equal to that of a sample mutually agreed upon by buyer and seller.

	Minimum	Maximum
Coarse particles:	Per cent	Per cent
Retained on Standard No. 200[2] screen..	.....	None
Retained on Standard No. 325[2] screen...	.....	2.0
Lead carbonate	65.0	75.0
Total impurities, including moisture....	.....	2.0

[1]Prepared and recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization August 11, 1919. P. H. Walker, Bureau of Standards, Chairman; H. E. Smith, U. S. Railroad Administration, Secretary. Circular of the Bureau of Standards. No. 84.

[2]The No. 200 and No. 325 screens are the same as screens formerly known as 200-mesh and 350-mesh.

(b) Paste

The paste shall be made by thoroughly grinding the above described pigment with pure raw or refined linseed oil.

The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Minimum	Maximum
	Per cent	Per cent
Pigment	90	92
Linseed oil	8	10
Moisture and other volatile matter	.....	0.7
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	.....	2.0

2. Sampling

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole.

With the dry pigment, this package shall be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test. When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

Whenever possible, an original unopened container shall be sent to the laboratory with the

paste; and when this is for any reason not done, the inspector shall determine by testing thoroughly with a paddle or spatula whether the material meets the requirement regarding not caking in the container. (See 4 (*a*).) After assuring himself that the paste is not caked, the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

Samples will in general be tested by the following methods, but the purchaser reserves the right to apply any additional tests, or use any available information to ascertain whether the material meets the specification.

3. Laboratory Examination of Dry Pigment

(a) Color

Take 1 gram of the sample, add 10 to 12 drops linseed oil, rub up on a stone slab or glass plate with a flat bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 1 gram of the standard basic carbonate white lead. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as white or whiter than the "standard," it passes this test. If the standard is whiter than the sample, the material does not meet the specification.

(b) Color Strength

Weigh accurately 0.01 gram of lampblack, place on a large glass plate or stone slab, add 5 drops of linseed oil, and rub up with a flat bottomed glass pestle, or muller, then add exactly 10 grams of the sample and 45 drops of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp edged spatula and grind out two more times in a like manner, giving the pestle a uniform pressure. Treat another 0.01 gram of the same lampblack in the same manner, except that 10 grams of standard basic carbonate white lead is used instead of the 10 grams of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light or lighter in color than the standard, it passes this test. If the standard is lighter in color than the sample, the material does not meet the specification.

(c) Coarse Particles

Dry in an oven at 105° to 110° C. a No. 200 and a No. 325 sieve, cool and weigh accurately. Weigh 100 grams of the sample; dry at 100° C., transfer to a mortar, add 100 c.c. kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene first through the 200 and then through the 325 sieve, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles which are too coarse to pass the sieves have been washed through, wash all kerosene from the sieves with ether or petroleum ether, heat the sieves for one hour at 105 to 110°

C., cool and weigh. The increase in weight of the 200 sieve should be not more than 0.020 gram and of the 325 sieve not more than 2.000 grams.

(d) Qualitative Analysis

Test for matter insoluble in acetic acid, zinc, calcium, etc., by the regular methods of qualitative analysis.

(e) Moisture

Place 1 gram of the sample in a tared wide mouth short weighing tube provided with a glass stopper. Heat with stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool and weigh. Calculate loss in weight as moisture.

(f) Total Lead and Insoluble Impurity

Weigh 1 gram of the sample, moisten with water, dissolve in acetic acid. If any insoluble residue remains, filter, dry at 105 to 110° C. and weigh as insoluble impurity. Dilute the solution to about 200 c.c., make alkaline with NH_4OH, then acid with acetic acid, heat to boiling and add 10 to 15 c.c. of a 10 per cent solution of sodium bichromate or potassium bichromate, and heat until the yellow precipitate assumes an orange color. Let it settle and filter on a Gooch crucible, washing by decantation with hot water until the washings are colorless, and finally transferring all the precipitate. Then wash with 95 per cent ethyl alcohol and then with ethyl ether; dry at 100° C. and weigh $PbCrO_4$. Calculate to lead oxide ($PbCrO_4 \times 0.69$

= PbO). Total lead may be determined by the sulphate method if preferred.

(g) Carbon Dioxide

Determine by evolution with dilute acid and absorption in soda lime or KOH solution, calculate CO_2 to $PbCO_3$, subtract PbO equivalent from total PbO and calculate residual PbO to $Pb(OH)_2$.

$$CO_2 \times 6.072 = PbCO_3$$
$$CO_2 \times 5.072 = PbO$$
$$PbO \times 1.197 = PbCO_3$$
$$PbO \times 1.08 = Pb(OH)_2$$

4. Laboratory Examination of Paste

(a) Caking in Container

When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of white lead paste. The paste shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(b) Mixing with Linseed Oil

One hundred grams of the paste shall be placed in a cup, 30 c.c. linseed oil added slowly with careful stirring and mixing with a spatula or paddle.

The resulting mixture must be smooth and of good brushing consistency.

(c) Moisture and Other Volatile Matter

Weigh accurately from 3 to 5 grams of the paste into a tared flat bottomed dish, about 5 cm. in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool and weigh. Calculate loss in weight as percentage of moisture and other volatile matter.

(d) Percentage of Pigment

Weigh accurately about 15 grams of the paste into a weighed centrifuge tube. Add 20 to 30 c.c. "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, add enough of the reagent to make a total of 60 c.c. in the tube. Place the tube in the container of a centrifuge, surround with water and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 c.c. of the extraction mixture, and once with 40 c.c. of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C., or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment.

(e) Examination of Pigment

Grind the pigment from (*d*) to a fine powder, pass through a No. 80 sieve to remove any "skins,"

preserve in a stoppered tube and apply tests 3(*a*), 3(*b*), 3(*d*), 3(*f*), and 3(*g*).

(f) Preparation of Fatty Acids

To about 25 grams of the paste in a porcelain casserole, add 15 c.c. of aqueous sodium hydroxide (see reagents) and 75 c.c. of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 c.c. of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 c.c. will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and lead sulphate precipitate, wash once with water; then add 50 c.c. of water and 50 c.c. of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 c.c. portion of water and then with 5 c.c. portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask, add 25 to 50 grams of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100-c.c. Erlenmeyer flask. Pass a rapid

current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat at a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

Note.—It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(g) Test for Mineral Oil

Place 10 drops of the fatty acid (*f*) in a 50 c.c. test tube, add 5 c.c. of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 c.c. of water and mix. A clear solution indicates absence of more than a trace of unsaponifiable matter. If the solution is not clear, the oil is not pure linseed oil.

(h) Iodine Number of Fatty Acids

Place a small quantity of the fatty acids 4 (*f*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 gram (0.10 to 0.20 gram) to a 500-c.c. bottle having a well ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 c.c. of chloroform. Whirl the bottle to dissolve the sample. Add 10 c.c. of chlorofrom to two empty bottles like that used for the sample. Add to each bottle 25 c.c.

of the Hanus solution (see reagents) and let it stand with occasional shakings for one-half hour. Add 10 c.c. of the 15 per cent potassium iodide solution and 100 c.c. of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titration on the two blank tests should agree within 0.1 c.c. From the difference between the average of the blank titrations and the titration on the sample, and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 gram of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(i) Coarse Particles and "Skins"

Weigh an amount of paste containing 100 grams of pigment (see 4 (*d*)), add 100 c.c. kerosene, wash through a No. 325 screen and weigh the residue as in 3 (*c*). The total residue left on the screen should be not more than 2.0 grams.

5. Reagents

(a) Extraction Mixture

10 volumes ether (ethyl ether)
6 volumes benzol
4 volumes methyl alcohol
1 volume acetone

(b) Aqueous Sodium Hydroxide

Dissolve 100 grams sodium hydroxide in distilled water and dilute to 300 c.c.

(c) Standard Sodium Thiosulphate Solution

Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 grams crystallized sodium thiosulphate to 1000 c.c. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine.[1] This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(d) Starch Solution

Stir up 2 to 3 grams of potato starch or 5 grams of soluble starch with 100 c.c. of 1 per cent salicylic acid solution, add 300 to 400 c.c. of boiling water, boil the mixture until the starch is practically dissolved, and then dilute to one liter.

(e) Potassium Iodide Solution

Dissolve 150 grams potassium iodide free from iodate in distilled water and dilute to 1000 c.c.

(f) Hanus Solution

Dissolve 13.2 grams of iodine in 1000 c.c. of glacial acetic acid, 99.5 per cent, which will not reduce chromic acid. Add enough bromine, about 3 c.c., to double the halogen content, which is determined by titration. The iodine may be dissolved by applying heat, but the solution should be cold when the bromine is added.

[1]See Treadwell-Hall Analytical Chemistry, II, 3d ed., p. 646.

(g) Alcoholic Sodium Hydroxide Solution

Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 grams per 1000 c.c. Let the solution stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 grams to 1000 c.c.), kept at about 50° C. for 15 days, and then distilled.

CHAPTER XI

ELECTROLYTIC DEPOSITION OF LEAD

Lead may be determined electrolytically in a very rapid manner by following the procedure as outlined by Smith[1] in his Electro-Analysis.

The Rapid Precipitation of Lead Dioxide with the Use of a Rotating Electrode

"Twenty c.c. of concentrated nitric acid were added to a solution of lead nitrate, giving a total volume of about 125 c.c. and acted upon with a current of $N.D._{100} = 10$ amperes and 4.5 volts. The rotating electrode (cathode) performed 600 revolutions per minute. The deposits had a uniform, velvety black color. There was no tendency on the part of the deposit to scale off, though more than a gram of the dioxide was precipitated. The time varied from ten to fifteen minutes. A platinum dish with sand blasted inner surface was used as an anode.

By using a current of $N. D._{100} = 11$ amperes and 4 volts upon a solution of lead nitrate containing 0.4996 gram of lead or 0.5787 gram of dioxide, the rate of precipitation was found to be:

In 5 minutes..0.4940 gram lead dioxide.
In 10 minutes..0.5708 gram lead dioxide.
In 15 minutes..0.5747 gram lead dioxide.

[1]Electro-Analysis, Smith: P. Blakiston's Sons & Co.

In 20 minutes..0.5770 gram lead dioxide.
In 25 minutes..0.5787 gram lead dioxide.
In 30 minutes..0.5789 gram lead dioxide.

The maximum time period for a quarter of a gram of metal is fifteen minutes, and the maximum time for a half gram of metal is twenty-five minutes."

CHAPTER XII

STANDARD METHODS OF CHEMICAL ANALYSIS OF PIG LEAD[1]

A. Determination of Silver

Weigh 100 grams of the sample into a 3 inch scorifier and heat in a muffle furnace until the assay "covers." Pour into an iron mold and allow to cool. Free the resulting lead button from PbO, scorify again and pour as before. The button last obtained should not weigh over 20 grams and can be cupelled directly. Weigh the silver button obtained upon an assay balance.

Note.—If the amount of silver is large, the button should be examined for gold, in the usual manner.

B. Determination of Bismuth

Solutions Required

Sodium Carbonate.—Dissolve 100 grams Na_2CO_3 in a liter of distilled water.

Ammonium Carbonate.— Make a half saturated solution.

Alkaline Sulphide Wash Solution.— Dissolve 200 grams of KOH in a liter of distilled water and mix one part of this solution with 4 parts of H_2S water.

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[1]Reprinted by permission from the 1921 Book of the A. S. T. M. Standards of the American Society for Testing Materials.

Method

(*a*) Determination for Ordinary Amounts of Bismuth.

Dissolve 20 grams of the sample in a 400-c.c. beaker with 100 c.c. of HNO_3 (1:4), with the aid of heat. When solution is complete, add dilute ammonia (1:2) with constant stirring, drop by drop from a burette, until a faint opalescence appears. If an actual precipitate is formed, redissolve by the addition of a small amount of HNO_3 (1:4) and repeat the addition of ammonia. Now add 5 c.c. of HCl (1:9), fill the beaker with hot water, bring to boiling, and allow to stand on a steam bath for two hours. The assay, while standing, must not reach the boiling temperature. Filter through a 7-cm. paper. Transfer the precipitate completely to the paper by means of a " policeman" and wash twice with hot water. Carefully examine the filtrate, washings, and any decanted liquid and reject if clear. Dissolve the precipitate by dropping around the edges, from a 5-c.c. pipette, 5 c.c. of boiling HCl (1:9), receiving the solution in the original beaker. Wash the paper thoroughly with hot water, fill the beaker with water, bring to boiling, and allow to stand as before. Filter the bismuth oxychloride upon a weighed Gooch crucible, wash thoroughly with water, once with alcohol, once with ether, and dry upon the hot plate. Cool and weigh.

Note.—If time permits, it is convenient to allow the assay to stand over night. In that case, the precipitate of bismuth oxychloride generally settles so completely that the clear supernatant solution can be decanted.

(*b*) Determination for Amounts of Bismuth Smaller Than Can Be Determined by (*a*).

Dissolve 100 grams of the sample in 500 c.c. of dilute HNO_3 (1:4). When solution is complete, allow to cool and add Na_2CO_3 solution little by little until a slight permanent precipitate has formed. Then add 50 c.c. of the Na_2CO_3 solution, bring to boiling, allow to stand warm until the supernatant liquor is clear again, filter and reject the filtrate. Dissolve the precipitate without washing by slowly pouring hot HNO_3 (1:4) around the edges of the filter paper, using no more acid than necessary. Wash the paper once with hot water and determine bismuth in the filtrate as described in (*a*).

Note.—When the sample contains a small amount of bismuth, it is often difficult to ascertain when the correct amount of ammonia has been added to the nitrate solution. In this case, place a small piece of litmus paper in the solution and add the ammonia very gradually until the litmus paper indicates a neutral reaction.

(*c*) Determination of Bismuth in Samples Containing Appreciable Amounts of Tin and Antimony.

Use a piece of litmus paper as in Note under *(b),* and after the first precipitation of bismuth oxychloride has been filtered off and washed (see (*a*)) proceed as follows: Dissolve the bismuth by dropping around the edges of the paper 10 c.c. of boiling HCl (1:2), receiving the solution in the original beaker. Discard the paper after washing. Dilute the solution to about 200 c.c. with fresh H_2S water and then pass H_2S gas through the hot solution for fifteen minutes. Filter and wash with

hot water. Remove any tin or antimony present by washing three times with alkaline sulphide wash solution. Wash the precipitate again with hot water, place it, together with the filter paper, in a 100-c.c. beaker, add 20 c.c. of HNO_3 (1:4), boil until sulphides are completely dissolved and the paper well pulped. Filter the solution, receiving the filtrate in the original beaker, and wash well. Determine bismuth in the filtrate as in (*a*).

Notes.—When the sample contains comparatively large amounts of tin or antimony, the residue left after the solution of the lead in the nitric acid obscures the opalescence found upon the addition of ammonia.

If the original sample contains more than 0.25 per cent of bismuth, it is preferable to use only a 10 gram charge.

C. Determination of Arsenic

Method

Dissolve 111.11 grams of the sample in 550 c.c. of HNO_3 (1:4). When solution is complete wash into a graduated liter flask. Add 75 c.c. of H_2SO_4 (1:1), cool, and make up to the mark with water. Transfer to a large beaker, rinsing out the flask with 25 c.c. of water. Mix thoroughly, allow to settle and filter off 900 c.c., equivalent to a 100 gram charge. Evaporate in a large porcelain dish until only enough H_2SO_4 is left to moisten the residue. When cool, wash into a small distilling flask with 60 c.c. of HCl (specific gravity 1.20) and 20 c.c. of water, cleaning the dish carefully. Add 10 grams of ferrous sulphate and distill, boiling to as small volume as possible. When cool add 50 c.c. more HCl (specific gravity 1.20) and redistill. Pass H_2S gas through the cold distillate for 45 minutes. Filter, and weigh the As_2S_3 on a Gooch

crucible, washing in cold water, alcohol and CS_2. After drying and weighing, redissolve with $(NH_4)_2CO_3$ solution and reweigh the Gooch crucible, calculating the loss in weight to arsenic.

Note.—The 25 c.c. of water added is equivalent to the volume of precipitated lead sulphate.

D. Determination of Remaining Metals

Solutions Required

Tartaric Acid.— Dissolve 50 grams of tartaric acid in 250 c.c. of distilled water to which has been added 250 c.c. HCl (specific gravity 1.20).

Method

Dissolve 222.23 grams of the sample in 1100 c.c. of HNO_3 (1:4), using a 1300-c.c. beaker. When solution is complete examine for color and turbidity. If clear, wash the solution at once into a 2000-c.c. graduated flask. In case of a residue (Note 1), however, dilute to about 1100 c.c. and allow to stand until the supernatant liquor is clear. Decant as much as possible into a 2000-c.c. flask, filter the remainder and receive the filtrate in the same flask. Wash the precipitate well and then place it, together with the filter paper, in a 100-c.c. beaker and add 20 c.c. of the tartaric acid mixture. Heat to boiling and when the paper is well pulped allow to digest warm for 30 minutes. Now add 50 c.c. of hot water, filter and wash. (Note 2.) Carefully dry the residue and ignite. If any appreciable residue remains, brush it into a small silver dish containing 1 gram of molten KOH. Fuse for 5 minutes, and after cooling dissolve in

as little hot water as possible and add to the above mentioned tartaric acid filtrate. Render this solution just alkaline with ammonia and then just acid with HCl, and saturate hot with H_2S gas. After digesting for 30 minutes on the steam bath, pass H_2S through the solution again for 15 minutes. Filter and wash with slightly acidified H_2S water. Reject the filtrate. Wash the sulphides from the paper into the original beaker and add 5 c.c. of KOH solution (1:5) for every 25 c.c. volume present. Digest hot for 5 minutes and filter through the original paper into a small flask graduated to 110 c.c. After washing with H_2S water containing a little of the KOH solution, cool the filtrate and make up to the mark. Mix and reserve 100 c.c. as alkaline sulphide solution No. 1. The precipitate may be discarded.

Add slowly to the main solution in the 2000-c.c. flask 150 c.c. of H_2SO_4 (1:1). After cooling and filling up to the mark, pour into a clean 3-liter flask provided with a rubber stopper. Rinse the flask out with 50 c.c. of water, which is equivalent to the volume of lead sulphate present and is added to the portion. After mixing thoroughly by shaking, allow the precipitate to settle and filter off 1800 c.c. of the liquid. This is equivalent to a 200 gram charge. Place this in a No. 9 porcelain evaporating dish and evaporate, first over a free flame and later on the hot plate until only enough H_2SO_4 is left to moisten the residue remaining. Add 50 c.c. of water and, after digesting warm for a short time, wash the solution into a 250-c.c.

beaker, cleaning the dish carefully. Allow the solution to digest on the steam bath for 4 or 5 hours. (Note 3.) Then filter, wash and evaporate the filtrate to 200-250 c.c. Place any residue (Note 4), together with the filter paper, in a 100-c.c. beaker and treat with 20 c.c. of the tartaric acid mixture. Boil for 5 minutes, dilute with 50 c.c. of hot water and filter. Make the filtrate alkaline with ammonia and just acid with HCl, and obtain the tin, antimony and arsenic as previously described, reserving the whole of the alkaline sulphide solution as solution No. 2. Reject the sulphide residue.

To filtrate from the lead sulphate, add ammonia until the neutral point is reached, and then for every 50 c.c. of the solution present add 2 c.c. of HCl (specific gravity 1.20). Pass H_2S gas into the hot solution until saturated, digest for 30 minutes on the steam bath and again pass H_2S gas into the solution. Filter and wash with H_2S water slightly acidified. (Note 5.) Separate tin, antimony and arsenic in the precipitate with KOH solution as usual, obtaining an alkaline sulphide solution No. 3. (Note 6.)

To sum up, three alkaline sulphide solutions have been obtained, containing tin, antimony and arsenic, a precipitate of metallic sulphides containing copper, lead, etc., and a solution containing iron, zinc, nickel, etc.

Notes.—1. A residue indicates the presence of antimony, tin possibly arsenic, or sulphur as lead sulphate.

2. It has been found that even this treatment occasionally fails to dissolve stannic acid completely.

3. If it is preferred, allow solution to stand over night to insure the complete solution of all soluble salts.

4. Any residue of lead sulphate may contain some tin, antimony, or possibly arsenic.

5. The filtrate will contain any iron, zinc, nickel, cobalt and manganese; while in the precipitate will be found any copper, cadmium, lead, silver, bismuth, tin, antimony and arsenic.

6. When separating the sulphides of arsenic, antimony and tin from sulphides of copper, lead, etc., it is necessary to wash all the sulphides back into the beaker in which they were precipitated. These sulphides sometimes cling so tenaciously to the paper that in dislodging them more water than the 25 c.c. specified is required. In this case allow the sulphides to settle and then decant the clear supernatant liquor through the filter until the volume is reduced to 25 c.c. Before rejecting decanted fluid always test with H_2S water.

In washing sulphide precipitates with water, much trouble is experienced from the tendency of the precipitate to pass through the filter in the colloidal form. This is particularly true in washing sulphides that have been digested with KOH. Time and trouble will be saved by washing all the sulphides precipitated from mineral acid solutions with H_2S water containing a little of the acid in which they were precipitated. The same is true of sulphides precipitated in or filtered from alkaline solution.

When working with alkaline solutions in which tin is to be determined, avoid the use of Jena or other glass that contains zinc. The zinc content of the glass may influence the result.

Determination of Antimony and Tin

Solutions Required

Potassium Iodide.— Dissolve 100 grams in a liter of distilled water.

Standard Sodium Thiosulphate.— Dissolve 24.8 grams of $Na_2S_2O_3.5H_2O$ in 1000 c.c. of distilled water, and allow to stand for 24 hours. Standardize against Antimony Metal, c. p., using same quantity of reagents and same procedure as under method. Each cubic centimeter is equivalent to approximately 0.006 gram of antimony.

Method

Wash the alkaline sulphide solutions Nos. 1, 2, and 3 into a 600-c.c. beaker, and acidify with 5 c.c. of HNO_3 (specific gravity 1.42) and 20 c.c. of HCl

(specific gravity 1.20). Evaporate the solution to dryness on the steam bath. Dissolve the residue in 200 c.c. of water, add 10 grams of oxalic acid and 10 grams ammonium oxalate and heat the solution until it is clear. Then pass H_2S gas through the boiling solution for 45 minutes. Filter off the precipitate, consisting of arsenic and antimony sulphides, and wash with hot water. Determine tin electrolytically in the filtrate, continuing the electrolysis until all the oxalic acid is decomposed and the solution becomes alkaline. Dissolve the deposit on the cathode with a small amount of HCl and examine qualitatively for tin.

Dissolve the sulphides of arsenic and antimony in KOH as usual, collecting the filtrate in a 500-c.c. Erlenmeyer flask. Add 50 c.c. of HCl (specific gravity 1.20) and boil the solution until about 30 c.c. are left. Expel the arsenic as chloride. Now oxidize the solution with a pinch of $KClO_3$ and boil until no more chlorine remains. Cool and add 5 c.c. potassium iodide solution. Titrate the liberated iodine with N/10 sodium thiosulphate solution, using carbon disulphide as an indicator.

Determination of Copper and Cadmium

Solutions Required

Sodium Chloride (Solution No. 1).— Dissolve 1 gram NaCl in 100 grams distilled water.

Sodium Chloride (Solution No. 2).— Dissolve 10 grams NaCl in 100 grams distilled water.

Standard Potassium Cyanide.— Dissolve 2 grams of KCN in a liter of distilled water and

standardize against a known amount of copper as treated in the analysis.

Sodium Carbonate (Solution No. 1).— Dissolve 50 grams Na_2CO_3 in 1 liter of distilled water.

Sodium Carbonate (Solution No. 2).— Dissolve Na_2CO_3 in distilled water to saturation.

Method

(*a*) Determination Where Copper Exceeds 0.0025 per cent.

Place the filter containing the sulphides in a 100-c.c. beaker and add 20 c.c. of HNO_3 (1:4). Heat with occasional stirring until the paper is thoroughly pulped and the sulphides are completely dissolved. Filter into a 250-c.c. beaker. Dry the residue, which generally contains a small amount of copper, ignite in a porcelain crucible, boil with 5 c.c. of HNO_3 (1:1), and wash into the main portion, keeping the volume below 100 c.c. Render it strongly alkaline with ammonia, and add 5 grams of potassium cyanide, then saturate it in the cold with H_2S gas. (Note 1.) Filter the solution and evaporate the filtrate to a volume of 20 to 30 c.c. in a 4 inch porcelain casserole. Boil until solution is complete. Add 20 c.c. of H_2SO_4 (1:1) and evaporate the solution under a hood until dense fumes of H_2SO_4 escape. Cool, dilute, and warm until copper sulphate is all dissolved. Now filter, if necessary, into a 200-c.c. beaker, render just alkaline with ammonia, make acid by the addition of 3 c.c. of HNO_3 per 100 c.c. solution, and electrolyze for copper.

Dissolve the precipitate of sulphides in the usual manner with 20 c.c. of HNO_3 (1:4). Add 1 c.c. NaCl solution No. 1 to the solution, still containing the pulped filter, and digest for one-half hour. Filter off the AgCl, wash and reject. Make the filtrate, not exceeding 100 c.c., alkaline with a slight excess of Na_2CO_3 and add 5 grams of KCN. Digest for 1 hour. Filter and wash with Na_2CO_3 solution No. 1. Reject the precipitate of bismuth. Now add a few cubic centimeters of ammonium sulphide solution to the filtrate to precipitate any cadmium as yellow cadmium sulphide. Filter upon a weighed Gooch crucible and weigh as cadmium sulphide. (Note 2.)

Notes.—1. Copper remains in the solution while lead, silver and bismuth and cadmium are precipitated.

2. If an appreciable amount of cadmium sulphide is found, it should be converted to and weighed as cadmium sulphate, according to method for cadmium under Standard Methods of Chemical Analysis of Spelter (see page 130) of the American Society for Testing Materials.

(*b*) Determination Where Copper Is Less Than 0.0025 Per Cent.

Place the paper containing the sulphides in a porcelain crucible, dry carefully and ignite. When the carbon has been all burned off, cool and dissolve the residue in 5 to 10 c.c. of HNO_3 (1:1). After evaporating to a volume of 1 to 2 c.c., add 1 c.c. of H_2SO_4 (1:1). Then evaporate the solution until fumes appear, cool, dilute, add a few drops of NaCl solution No. 2, and filter off the lead sulphate and silver chloride. Again evaporate the filtrate until fumes of H_2SO_4 appear, and when cold, dilute and neutralize with Na_2CO_3 solution No.

2. Then add about six drops of concentrated ammonia and titrate the solution with standard KCN solution until the blue color is discharged.

The cadmium can be obtained by making this solution, titrated for copper, strongly alkaline, diluting a little, and adding 5 grams of KCN. Saturate the solution cold with H_2S gas, filter, discard the filtrate and treat the precipitate for cadmium as described in Method (*a*).

Determination of Iron

Method

Evaporate the filtrate containing iron, zinc, etc., to 100 c.c. and oxidize with a few drops of HNO_3. Separate the iron with ammonia as usual, making two separations, and receive the filtrate in a 500-c.c. Erlenmeyer flask. Redissolve the iron hydroxide with hot HCl (1:1) or dilute H_2SO_4 and determine the iron volumetrically by any of the standard methods.

Determination of Zinc

Method

Add to the filtrate from the iron hydroxide 1 c.c. of cochineal indicator, and render just neutral with HCl. Then add 15 drops of twice normal HCl for each 100 c.c. of the solution. Saturate cold with H_2S gas and allow the flask, loosely stoppered, to stand over night. Filter and wash with H_2S water acidified in the same manner as above described. Dry the precipitate of zinc sulphide, carefully ignite in a porcelain crucible and weigh as zinc oxide.

Determination of Nickel and Cobalt

Solutions Required

Hydrogen Sulphide Wash Water.— To each 100 c.c. of hydrogen sulphide water add 20 c.c. neutral ammonium acetate.

Method

Render the filtrate just alkaline with ammonia and saturate with H_2S. Heat to boiling and then make just acid with acetic acid, add 20 c.c. of neutral ammonium acetate solution, and boil until the sulphides of nickel and cobalt separate out. Filter and wash with warm H_2S wash water. Dry the precipitate and paper in a porcelain crucible and carefully ignite. If there is an appreciable amount of residue after ignition, dissolve by boiling with 10 c.c. of aqua regia, wash into a 250-c.c. beaker, add 10 c.c. of H_2SO_4 (1:1), evaporate until fumes appear, cool, dilute to 200 c.c., make alkaline with ammonia, and add 15 c.c. of concentrated ammonia. Then electrolyze the solution and weigh the nickel and cobalt as such.

Notes—If the amount of nickel and cobalt is small it can be weighed as oxide.

If the filtrate from the nickel and cobalt sulphides shows a brown color, it indicates that the precipitation has not been complete. In this case render the solution ammoniacal and repeat the above process.

Determination of Manganese

Solutions Required

Standard Potassium Permanganate.— Mix 10 c.c. N/10 $KMnO_4$ and 100 c.c. of distilled water. Each cubic centimeter is equivalent to approximately 0.00011 gram Mn.

Dilute Sulphuric Acid.— Add 25 c.c. concentrated H_2SO_4 to 1000 c.c. of distilled water.

Nitric Acid Wash.—Add 300 c.c. HNO_3 to 1000 c.c. of distilled water.

Method

Evaporate the filtrate, which should now contain only manganese, to dryness in a porcelain dish and heat carefully over an Argand burner until all the ammonium salts have been driven off. (Note 1.) After cooling, moisten the residue with a little HCl and warm until dissolved. Add 1 c.c. of H_2SO_4 (1:1) and evaporate the solution until fumes appear, continuing the fuming until nearly all the H_2SO_4 has been driven off. Cool, and add 50 c.c. of HNO_3 (1:3) and 0.5 gram of sodium bismuthate. (Note 2.) Boil the solution until the pink color is destroyed. If any manganese is precipitated, dissolve by the addition of a few cubic centimeters of a dilute sodium thiosulphate solution. In this case the solution must be again boiled until freed from all fumes. After cooling, add an excess of sodium bismuthate, stir a few minutes and filter through ignited asbestos into a 100-c.c. Nessler tube. Wash with dilute HNO_3 (Nitric Acid wash) and make the filtrate up to the mark. Into another similar tube put 100 c.c. of dilute H_2SO_4 which has been made very faintly pink with potassium permanganate solution. Now add standard solution of potassium permanganate from a burette until the color of the sample is exactly matched.

Notes—1. It is best to bake here over a Bunsen flame until all the organic matter has been destroyed.

2. The HNO_3 must be freed from nitrous fumes by passing a current of air through the acid for one-half hour.

CHAPTER XIII

STANDARD METHODS OF CHEMICAL ANALYSIS OF SPELTER[1]

The methods that follow are based on the Report of the Sub-Committee on Methods of Analysis of Non-Ferrous Alloys for the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society, approved by the Supervisory Committee on Standard Methods of Analysis of that Society.[2] These methods were originally proposed by Elliott and Storer[3] and Price,[4] whose work has been checked and elaborated by the members of the Committee of the American Chemical Society and of this Society.

The methods are those generally accepted in the United States for standard analysis in all the large laboratories of both producers and consumers of zinc and zinc products.

The Electrolytic and Lead Acid methods described below are believed to be of equal merit, so far as accuracy is concerned, but where laboratories are equipped for electrolysis the electrolytic method is preferred as a time saver.

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[1]Reprinted by permission from the 1921 Book of A. S. T. M. Standards of the American Society for Testing Materials. Adopted, 1911; Revised and Printed as Separate Standard, 1921.

[2]Journal of Industrial and Engineering Chemistry, Vol. 7, 1915, p. 547.

[3]Memoirs, Am. Acad. Arts and Sciences, 8, Part 1, May 20 (1860).

[4]The Chemical Engineer, 9 (1909), 4.

Determination of Lead by the Electrolytic Method

Apparatus

Platinum cylindrical gauze electrodes containing approximately 400 meshes per sq. cm. (50 meshes per linear inch) are recommended for anode and cathode. They should be stiffened by doubling the gauze for about 3 mm. at the top and bottom of the cylinders. The anode should be approximately 30 mm. in diameter and 30 mm. in height. The stem should be made from 1.14 mm. or 1.29 mm. wire, flattened and electrically welded the entire width of the gauze; the height over all should be approximately 130 mm., and the gauze should be sand blasted. The cathode should be approximately 12 mm. in diameter by 30 mm. in height, the stem being of the same dimensions and welded in the same way as the anode.

Method

Place 8.643 grams (Note 1) of the sample in a 400-c.c. beaker, add sufficient water to cover and then add 30 c.c. HNO_3 (specific gravity 1.42) gradually. When action is complete, boil the solution for 10 minutes, wash off the watch glass and transfer the solution to a 200-c.c. electrolytic beaker, washing out the original 400-c.c. beaker. Dilute to 125 c.c. and electrolyze (Note 2) with a current of five amperes for 45 minutes. (Note 3.) Test the solution for complete precipitation of lead by washing the watch glasses and sides of the beaker, increasing the depth of the solution about 12 mm. Continue the current for 15 minutes and if the newly exposed surface is still bright, wash the

anode (Note 4) three or four times with distilled water, once with alcohol, and then dry in an oven (Note 5) at 210° C. for 30 minutes, cool in a dessicator and weigh.

The weight of the deposited PbO_2 in milligrams, divided by 100, gives the percentage of lead (Note 6).

Notes.—1. The empirical factor weight, 8.643 grams, is used instead of the theoretical one (8.660 grams), as dried dioxide contains some adherent and included water, not entirely expelled.

2. Before electrolyzing, the beaker should be covered with split watch glasses to prevent loss by spraying.

3. The time required for complete deposition is usually 30 to 45 minutes. For small amounts of lead 30 minutes will be found sufficient.

4. The washing should be done immediately, as the deposit of PbO_2 tends to dissolve.

5. The anode may also be dried on a hot plate, although a drying oven is to be preferred.

6. The PbO_2 deposit can be readily removed by immersing the anode in hot dilute solution of HNO_3 to which oxalic acid has been added, or by covering with dilute HNO_3 and inserting a rod of copper.

Determination of Lead by the Lead Acid Method

Solutions Required

Lead Acid.— Pour 300 c.c. of H_2SO_4 (specific gravity 1.84) into 1800 c.c. of distilled water; dissolve 1 gram of lead acetate in 300 c.c. of distilled water and add to the acid solution with stirring. Allow to settle for several days and siphon off the clear solution through a thick asbestos pad. (Note 1.)

Nitric Acid.— Mix 1000 c.c. of HNO_3 (specific gravity 1.42) with 1000 c.c. of distilled water.

Alcohol.— Mix 1000 c.c. of ethyl alcohol (95 per cent) with 1000 c.c. of distilled water.

Method

Place sample (Note 2) of 25, 15, 10, or 5 grams in a 350-c.c. beaker and add 300, 180, 120, or 60 c.c., respectively, of lead acid. After all but about 1 gram is dissolved, filter on a close filter and wash out the beaker twice with lead acid from a wash bottle. Wash the undissolved matter from the filter into the original beaker with water and dissolve with 10 c.c. of HNO_3. Add 40 c.c. of lead acid, and evaporate until copious fumes of H_2SO_4 are evolved. When cool, add 35 c.c. (Note 3) of water, heat to boiling and add the first filtrate (Note 4), stir well and allow to stand over night (Note 5). Filter on a Gooch crucible, wash with lead acid, then with alcohol water mixture, and finally with alcohol alone. Set the Gooch crucible inside of a larger porcelain crucible (Note 6) and heat for five minutes at the full heat of a Tirrill burner. Cool and weigh as $PbSO_4$.

Notes.—1. When lead acid is used, it is unnecessary to consider the solubility of $PbSO_4$, since the solution is always brought back to the same volume as the lead acid used originally, consequently it will retain no $PbSO_4$ from the sample.

2. The amount of sample taken is governed by the grade of spelter:

Grade No. 1, 25 grams. Grade No. 3, 10 grams.
Grade No. 2, 15 grams. Grade No. 4, 5 grams.
Grade No. 5, 5 grams.

3. The 35 c.c. of water added is the quantity of water evaporated from the lead acid.

4. The first filtrate, which contains the greater part of the zinc, may also contain a small amount of $PbSO_4$.

5. It is preferable to allow the solution and precipitate of $PbSO_4$ to stand over night, although this time may be shortened to not less than five hours.

6. The Gooch crucible is heated inside of a porcelain crucible to avoid reduction of the $PbSO_4$ by flame gases and mechanical disintegration of the asbestos mat.

Determination of Iron

Solution Required

Dilute Ammonia Water.—Mix 100 c.c. of NH_4OH (specific gravity 0.90) with 1000 c.c. of distilled water.

Sulphuric Acid (1:4).— Mix 250 c.c. of H_2SO_4 (specific gravity 1.84) with 1000 c.c. of distilled water.

Sulphuric Acid (1:1).— Mix 500 c.c. of H_2SO_4 (specific gravity 1.84) with 500 c.c. of distilled water.

Dilute Sulphuric Acid for Reductor.— Mix 50 c.c. of H_2SO_4 (specific gravity 1.84) with 1000 c.c. of distilled water. This solution is used boiling hot.

Potassium Permanganate.— Dissolve 0.2 gram of $KMnO_4$, c. p., in 1000 c.c. of distilled water. Allow to stand for several days in a glass stoppered bottle in a dark closet and then filter through prepared asbestos. Standardize against 0.020 gram portions of pure sodium oxalate, dissolved in 200 c.c. of the dilute H_2SO_4 for reductor. Each cubic centimeter of $KMnO_4$ is equivalent to approximately 0.00033 gram of iron.

Method

Place 25 grams of the sample in a tall 700-c.c. beaker and dissolve cautiously with 125 c.c. of HNO_3 (specific gravity 1.42). Boil, dilute to about 300 c.c., add 10 grams of NH_4Cl and then ammonia water (specific gravity 0.90) until the precipitated $Zn(OH)_2$ has redissolved. Boil, let settle and fil-

ter on an 11-cm. filter paper (Note 1). Wash with dilute ammonia water and then with hot water until free from chlorides. Dissolve precipitate from the paper with hot H_2SO_4 (1:4), add 40 c.c. of H_2SO_4 (1:1), cool, and pass through a Jones reductor (Note 2). Wash out the reductor first with 150 c.c. of dilute H_2SO_4 for reductor and then with 100 c.c. of distilled water and titrate with a standard $KMnO_4$ solution (Note 3).

Notes.—1. A filter paper which will retain $Fe(OH)_3$ and filter rapidly should be used. Whenever the amount of iron is at all large or when great accuracy is demanded, a second precipitation of $Fe(OH)_3$ should be made by dissolving the precipitate on the paper in hot dilute HCl, adding ammonia water and filtering, in order to remove all traces of nitrates.

2. The reductor should be clean, preferably washed out with 150 c.c. of dilute H_2SO_4 and 100 c.c. of water first. If, before passing through the reductor, a large amount of $PbSO_4$ is present, it is well to filter it off so as to prevent it from clogging the reductor. A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the body of the reductor. For description and further details of use of reductor, see "The Chemical Analysis of Iron," by A. A. Blair, or "Quantitative Chemical Analysis," by H. P. Talbot.

3. A blank determination should be made on corresponding amounts of acid and water passed through the reductor and the results should be corrected accordingly. About 0.5 c.c. of the $KMnO_4$ solution will be required to give a permanent coloration to the solution.

Determination of Cadmium Gravimetrically

Solutions Required

Sulphuric Acid (1:1).— Mix 500 c.c. of H_2SO_4 (specific gravity 1.84) with 500 c.c. of distilled water.

Sulphuric Acid (1:5).— Mix 200 c.c. of H_2SO_4 (specific gravity 1.84) with 1000 c.c. of distilled water.

Hydrochloric Acid (1:3).— Mix 250 c.c. of HCl (specific gravity 1.20) with 750 c.c. of distilled water.

Method

Place 25 grams of drillings in a tall 500-c.c. beaker; add 250 c.c. of water and 55 c.c. of HCl (specific gravity 1.20) and stir. When the action has almost ceased add more acid with stirring, using about 2 c.c. at a time and allowing to stand after each addition, until finally all but about 2 grams of the zinc has been dissolved. (Note 1.) Filter, first transferring one of the undissolved pieces of zinc to the filter, and wash twice with water. Discard the filtrate. Wash the undissolved matter on the filter paper into the 500-c.c. beaker, cover and dissolve in 10 c.c. of water and 10 c.c. of HNO_3 (specific gravity 1.42). Transfer to a casserole, add 20 c.c. of H_2SO_4 (1:1) and evaporate until fumes appear. Take up with 100 c.c. of water, boil, cool, and let settle over night. (Note 2.) Filter off the $PbSO_4$ on paper, wash twice with water, retain the filtrate but discard the paper and precipitate. Dilute the filtrate to 400 c.c., add about 10 grams of NH_4Cl, and pass H_2S gas through for 1 hour (Note 3). Allow to stand until the precipitate has settled, and filter off the impure CdS (Note 4) on a loose-bottom Gooch crucible. Remove the precipitate by punching out the bottom into a tall 200-c.c. beaker, wiping off the sides of the crucible with a little asbestos pulp. Add 60 c.c. of H_2SO_4 (1:5) and boil for 30 minutes (Note 5). Filter, wash, and dilute to 300 c.c., add about 5 grams of NH_4Cl and precipitate with H_2S gas as before (Note 6). Repeat, making a third precipitation if the amount of cadmium present is

large (Note 7). After the final precipitation, let settle, filter and transfer to a weighed platinum dish, cover, and dissolve in HCl (1:3). Dissolve the precipitate remaining on the paper in hot HCl (1:3) and add also to the solution in the platinum dish (Note 8). Add 10 c.c. of H_2SO_4 (1:1) and evaporate the solution until copious fumes are evolved (Note 9). Remove the excess of H_2SO_4 by heating the dish cautiously, and finally heat to between 500 and 600° C. Cool and weigh as $CdSO_4$.

Notes. -1. The addition of HCl will dissolve the zinc and a small amount of the cadmium. By adding the acid in small quantities, i. e., keeping the acidity low, and also keeping the solution cold, the amount of cadmium dissolved will be small. Since it requires some time to completely reprecipitate any cadmium dissolved, it is desirable for the solution to stand over night following the addition of the 55 c.c. of HCl at the start. For the same reason the solution should be allowed to stand after the last addition of acid, and care be taken that the stated amount of spelter remain in the undissolved residue. If the solution is heated, or if time is not allowed for the action of the acid to cease completely, small amount of cadmium may pass into the solution and be lost.

Equally satisfactory, or in some cases more satisfactory results are obtained by using H_2SO_4 to dissolve the major portion of the zinc. The rate of solution is slower and the tendency for cadmium to pass into solution less. The quantity of acid required can be calculated, measured out at the beginning and small quantities added from time to time as the action becomes slow.

2. It is desirable to allow it to settle over night to precipitate all the $PbSO_4$ from the solution and to give good conditions for filtering.

3. It is occasionally necessary to add a drop or two of ammonia water to the solution to start the precipitation of CdS.

4. All the cadmium will be precipitated as sulphide together with some ZnS. The major portion of the zinc will remain in solution.

5. In case of high cadmium content, more acid may be required.

6. The second precipitation should give practically pure CdS.

7. A third precipitation will remove any uncertainty as to the completeness of the separation of cadmium from zinc.

8. A crucible may also be used if the volumes are kept small or evaporated before transferring to the crucible.

9. On evaporating to fumes, darkening of the solution may occur from filter paper shreds. This may be destroyed by diluting slightly with water and adding 5 c.c. HNO_3 (specific gravity 1.42) and again evaporating to fumes.

Determination of Cadmium by the Electrolytic Method

Solutions Required

Potassium Hydroxide (Note 1).— Dissolve 20 grams of KOH, c. p., in 200 c.c. of distilled water.

Potassium Cyanide (Note 2).— Dissolve 20 grams of KCN, c. p., in 200 c.c. of distilled water.

Apparatus

See "Determination of Lead by the Electrolytic Method."

The anode, as used in the lead determination, is here used as the cathode, and vice versa.

Method

See "Determination of Cadmium Gravimetrically."

Dissolve the final precipitate of CdS in hot HCl (1:3), boil to remove H_2S, adding a few drops of HNO_3 (specific gravity 1.42) near the end, and filter off the separated sulphur. Transfer the solution to a 200-c.c. electrolytic beaker, add a drop or two of phenolphthalein and then KOH solution until a permanent red color is obtained. Add KCN solution with constant stirring until the precipitate of $Cd(OH)_2$ is completely dissolved (Note 3). Dilute to 150 c.c. and electrolyze with a current of five amperes for two hours (Note 4). Test for completeness of deposition by washing the watch glasses and sides of the beaker to increase the depth of the solution. Continue electrolysis for twenty minutes and if the newly exposed surface

of the cathode is still bright, remove the beaker with electrolyte and wash the electrodes three times with distilled water and twice with ethyl alcohol (95 per cent). Dry the cathode at 100° C., cool and weigh. The increase is metallic cadmium.

Notes.—1. Pure NaOH may be used in place of KOH.
2. Pure NaCN may be used in place of KCN.
3. Avoid using an excess of KCN.
4. The test for completeness of deposition may be made after one hour when the quantity present is not large.

CHAPTER XIV

STANDARD METHODS OF CHEMICAL ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND COPPER[1]

These methods apply particularly to white metal bearing alloys (known commercially as "Babbitt Metal") and to similar lead and tin base alloys.

Two sets of methods are here given. The first method is somewhat slow but is recommended as giving the more accurate results where the analysis of these alloys is of comparatively infrequent occurrence. The second method is rapid and is suitable for control work, giving good results after the analyst has become familiar with it.

I. GENERAL METHOD[2]

A. Determination of Lead, Copper, Antimony and Tin

Determination of Lead

Solutions Required

Mixed Acid.— Dissolve 20 grams of KCl in 500 c.c. of water, add 400 c.c. of HCl (specific gravity 1.20), mix and add 100 c.c. of HNO_3 (specific gravity 1.42).

[1]Reprinted by permission from the 1921 Book of A. S. T. M. Standards of the American Society for Testing Materials.

[2]G. W. Thompson's method. See Journal, Soc. Chem. Ind. Vol. 15, p. 179.

Alcohol Hydrochloric Acid Mixture.— Mix 400 c.c. of 95 per cent ethyl alcohol and 100 c.c. of HCl (specific gravity 1.20).

Acid Ammonium Acetate.— To 500 c.c. of NH_4OH (specific gravity 0.90), add 500 c.c. of water and then acetic acid (80 per cent) until slightly acid to litmus.

Method

Dissolve 1 gram of the finely divided alloy by boiling in 70 to 100 c.c. of "mixed acid" solution in a covered beaker. Add more "mixed acid" if a complete solution of the alloy is difficult to obtain, and continue boiling until evaporated to about 50 c.c. Add 5 c.c. of HCl (specific gravity 1.20), cool in ice water until the bulk of $PbCl_2$ has crystallized out, then add slowly, with constant stirring, 50 c.c. of alcohol (95 per cent), continue stirring for a few minutes and cool in ice water for 10 minutes. Add 50 c.c. more alcohol from a pipette, allow to stand in ice water for 20 minutes and filter through 9-cm. paper into an 800-c.c. beaker. Wash by decantation three times with alcohol hydrochloric acid mixture and finally wash the paper twice with the same mixture. Wash the $PbCl_2$ from the paper back into the beaker; wash paper several times with hot water, catching washings in beaker with the bulk of the chloride. Finally wash paper with hot ammonium acetate solution. Heat until all $PbCl_2$ is dissolved. Add 15 c.c. of saturated solution of $K_2Cr_2O_7$; heat until precipitate is of good

orange color; filter on weighed Gooch crucible; wash with water, alcohol and ether; dry at 110° C. and weigh. Calculate percentage of lead by the empirical factor of 63.75.

Notes.—1. With proper manipulation, the $PbCl_2$ precipitate should contain consistently all but 0.003 grams of lead.

2. During the heating of the acid ammonium acetate to dissolve the $PbCl_2$, the solution should remain perfectly clear, any turbidity indicating the presence of tin or antimony, as even 1 milligram of tin or antimony will cause a slightly but distinct turbidity.

Determination of Copper and Antimony

Solutions Required

Potassium Hydroxide.— Dissolve 100 grams of KOH in 500 c.c. of water.

Potassium Cyanide.— Dissolve 3.5 grams of KCN in 1800 c.c. of water and standardize against copper of known purity.

Sodium Thiosulphate.— Dissolve 24.8 grams of $Na_2S_2O_3.5H_2O$ in 1000 c.c. of water, and allow to stand for 24 hours. Standardize against Antimony Metal, c. p., using same quantity of reagents and same procedure as under (c) Determination of Antimony.

Method

See "Determination of Lead."

Evaporate the filtrate from $PbCl_2$ filtration by boiling in the loosely covered 800-c.c. beaker, and finally take to dryness on a water bath. Add 10 c.c. of KOH solution and after a few minutes add 20 c.c. of 3 per cent H_2O_2. Add more KOH, if solution is acid, until an alkaline reaction is shown by litmus paper. Heat on the water bath for 20

minutes, add 10 grams of ammonium oxalate, 10 grams of oxalic acid, and 200 c.c. of water and heat to boiling. Pass in H_2S for 45 minutes with solution near boiling; filter at once; and wash precipitate with hot dilute solution of oxalic acid saturated with H_2S, catching washings with filtrate.

Wash the precipitate of copper and antimony sulphides from the filter paper back into the beaker with the least amount of water possible; treat with 10 c.c. of KOH solution; heat on water bath until the undissolved matter is distinctly black, filter through same paper into a 300-c.c. Erlenmeyer flask. Wash the precipitate with hot water containing a small amount of K_2S.

(a) Determination of Copper by Potassium Cyanide Titration

Dry and ignite the precipitate with paper in a small casserole, dissolve in nitric acid (specific gravity 1.42), boil to expel nitrous fumes, neutralize with Na_2CO_3, add a few drops of NH_4OH and titrate with standard KCN solution.

(b) Determination of Copper by Electrolytic Method

See "Determination of Copper by Potassium Cyanide Titration."

Dry and ignite the sulphide precipitate in a small casserole, dissolve in 10 c.c. of HNO_3 (specific gravity 1.42), boil until oxides of nitrogen are expelled and add 50 c.c. of distilled water. Transfer to a tall 200-c.c. beaker, wash out casserole, add 5 c.c. of H_2SO_4 (specific gravity 1.84) and determine cop-

per by electrolysis. See the determination of copper by the electrolytic method in the Standard Methods of Chemical Analysis of Manganese Bronze (Serial Designation: B 27) of the American Society for Testing Materials.

Notes.—1. On filter after heating with KOH solution, the copper remains as sulphide with a small amount of lead sulphide which failed to be precipitated as chloride. If it is desired to determine this lead, it can be done by separation from the copper by ordinary methods.

2. If the amount of antimony and copper is small (less than 10 milligrams) the lead which failed to be precipitated as chloride may also fail to come down as sulphide on passing H_2S through the oxalic solution. It will remain in the filtrate from the sulphides and be deposited electrolytically with the tin on the cathode. This can be prevented by adding an oxalic acid solution of a pure antimony salt containing about 100 milligrams of antimony just before passing H_2S. In this case antimony must be determined on a separate portion.

3. If the amount of copper present is from 8 to 10 milligrams or more, it should be determined by the electrolytic method. In this case the small amount of lead precipitated as sulphide with the copper is deposited on the anode as PbO_2 and may be weighed, calculated to lead by factor 86.43 and added to that obtained under "Determinations of Lead."

Determination of Antimony

See "Determination of Copper by Potassium Cyanide Titration."

Add 50 c.c. of HCl (specific gravity 1.20) to the KOH solution of antimony sulphide, and boil down to small volume until all arsenic has been expelled as arsenious chloride.

Add 25 c.c. of HCl (specific gravity 1.20) and 1 gram of $KClO_3$ and boil until colorless. Filter into a 300-c.c. Erlenmeyer flask, through glass wool if sulphur has separated, wash out original flask with HCl (specific gravity 1.20), cool, add 1 gram of KI, 1 c.c. of CS_2, and titrate with standard thiosulphate solution.

Determination of Tin

Apparatus for Electrolysis

Electrodes.— Cylindrical cathodes of platinum wire gauze, 2 by 1⅜ inches diameter.

Platinum wire spiral anodes.

Method

See "Determination of Copper and Antimony."

Concentrate the filtrate and washings from the precipitated sulphides, if necessary, to a volume of 200 c.c. and add 5 grams more of oxalic acid in case the amount of tin is over 0.5 gram. Electrolyze until the solution reacts alkaline, using a current of about 0.5 ampere. Remove the cylinder; wash twice with distilled water and once with 95 per cent ethyl alcohol; dry at 110° C. and weigh.

Note.—If the electrolysis is carried out over night it will usually be found by morning that the solution has become alkaline and it may be taken for granted that the tin has all been precipitated on the cathode. The best results are obtained by regulating the current, or the time, so as to render the solution alkaline only a very short time before the cathode is to be removed. The cathode should be placed close to the bottom of the beaker to insure proper agitation of the electrolyte.

B. Determination of Arsenic

Solutions Required

Ferric Chloride.— Solution of specific gravity 1.43.

Ammonium Carbonate.— Dissolve 75 grams in 500 c.c. of water.

Method

Weigh 1 gram of sample into a 250-c.c. distillation flask and add 10 c.c. of $FeCl_3$ solution, 60 c.c. of HCl (specific gravity 1.20), 20 c.c. of water and

5 grams of KCl. Connect the flask with a condenser, heat slowly until solution is complete and boil down to as small a volume as possible, catching distillate in a tall 400-c.c. beaker. Cool flask, add 50 c.c. HCl (specific gravity 1.20) and redistill as before, catching distillate in same beaker. Cool distillate and pass H_2S through for one hour, allow to settle and filter the arsenious sulphide on a Gooch crucible. Wash twice with HCl (1:4), four times with cold water, three times with alcohol and four times with CS_2. Dry at 110° C. for 10 minutes, and weigh after cooling. Dissolve the arsenious sulphide with $(NH_4)_2\ CO_3$ solution, wash thoroughly with water, dry for 30 minutes at 110° C. and reweigh after cooling. The difference in weights multiplied by 0.60911 gives the percentage of arsenic.

II. RAPID METHOD FOR CONTROL WORK[1]

A. Determination of Lead and Copper

Solutions Required

"Lead Acid."— Mix 300 c.c. of H_2SO_4 (specific gravity 1.84) and 1800 c.c. of distilled water. Dissolve 1 gram of lead acetate, c. p., in 300 c.c. of distilled water and add this to the hot solution,

[1]See "The Analysis of Alloys of Lead, Tin, Antimony and Copper," by D. J. Demorest, Journal Ind. and Eng. Chem., Vol. V, p. 842; "Rapid Analysis of Alloys for Tin, Antimony and Arsenic," by F. A. Stief, Journal Ind. and Eng. Chem., Vol. VII, p. 211; and "Technical Analysis of Brass," 1917. Price and Meade, p. 182.

stirring meanwhile. Let stand at least 24 hours and siphon through a thick asbestos filter.

Dilute Alcohol for Washing.— Mix equal parts of denatured alcohol and distilled water.

(a) **Determination of Lead**

In a covered 300-c.c. Erlenmeyer flask dissolve 1 gram of the alloy in 20 c.c. of H_2SO_4 (specific gravity 1.84); heat the solution nearly to boiling until the metal is completely decomposed and the $PbSO_4$ is white (this may take 30 minutes or more) and finally boil for several minutes. Allow to cool, but not below 60° C., and then add slowly 50 c.c. of water while the solution is agitated. Heat to boiling for several minutes in order to insure complete solution of antimony sulphate. Allow the $PbSO_4$ to settle out until the solution is clear, not letting the temperature fall below 60° C. If the liquid does not clear quickly it must be heated longer. When clear, pour solution through a weighed porcelain Gooch crucible with asbestos mat, decanting the solution as completely as possible without allowing more than a very small amount of $PbSO_4$ to go over into the crucible. Now add 10 c.c. more of H_2SO_4 (specific gravity 1.84) to the $PbSO_4$ in the original flask, and boil for several minutes. Cool, add slowly 30 c.c. of water, and again heat to boiling for a few minutes; allow the solution to cool to about 60° C. and completely transfer the $PbSO_4$ to the Gooch crucible. Wash with lead acid, retaining the filtrate and these washings for the copper determination. Remove the beaker containing these solutions and wash out

the lead acid with dilute alcohol; set the Gooch crucible inside a porcelain crucible; dry and ignite for five minutes at the full heat of a Tirrill burner; cool and weigh as $PbSO_4$, which contains 68.29 per cent lead.

(b) **Determination of Copper**

To the filtrate from the $PbSO_4$, which contains the copper and which has been transferred to an Erlenmeyer flask, add NH_4OH (specific gravity 0.90) until the solution is slightly alkaline; then add 2 c.c. of H_2SO_4 (specific gravity 1.84); heat nearly to boiling; add 2 grams of Na_2SO_3 and when this is entirely dissolved add 1 gram of KCNS dissolved in 10 c.c. of water. Shake well and allow the precipitated CuCNS to settle for one hour while the solution is kept hot. Filter on a close filter paper, wash with cold water and ignite paper and precipitate in a porcelain crucible. Proceed by one of the two following methods:

(1) Dissolve in HNO_3 (specific gravity 1.42), add 5 c.c. H_2SO_4 (specific gravity 1.84), evaporate until fumes of H_2SO_4 are evolved. Dilute to about 100 c.c. with distilled water. Add 1.5 c.c. of HNO_3 (specific gravity 1.42) and determine copper by electrolysis. See the "Determination of Copper by the Electrolytic Method," Standard Methods of Chemical Analysis of Manganese Bronze (Serial Designation: B 27) of the American Society for Testing Materials.

(2) Dissolving the ignited precipitate in HNO_3 (specific gravity 1.42), as in (1); boil to expel

nitrous fumes, neutralize with Na_2CO_3 and determine volumetrically with cyanide as in A of "General Method."

Note.—If the amount of copper is very small it may escape detection by this method, in which case it should be determined as in A of "General Method."

B. Determination of Arsenic, Antimony and Tin

Apparatus

Arsenic Still.— A condenser is made from glass tubing in the form of a letter S, about 18 in. long and ½ in. in inside diameter, tapering to about ¼ in. at the upper end and to about ⅛ in. at the lower end. One curve is nearly filled with water, and is submerged in cold water in a 500-c.c. beaker. The lower end dips into about 75 c.c. of water in a 300-c.c. beaker and the upper end is connected by a delivery tube with a 300-c.c. Florence flask, closed with a rubber stopper which is fitted with a delivery tube and with a thermometer reaching to about 1 in. above the surface of the liquid in the flask.

Solutions Required

Iodine.— Dissolve 10.7 grams of iodine in 50 c.c. of distilled water which contains 20 grams of KI in solution and dilute to 1000 c.c. with distilled water. Standardize against pure tin having exactly the same conditions for titration as are specified for the analysis of the alloy. Each cubic centimeter is equivalent to approximately 0.00500 gram of tin or 0.00315 gram of arsenic.

Potassium Permanganate.— Dissolve 2.7 grams of $KMnO_4$ in distilled water, filter through asbestos, and dilute to 1000 c.c. with distilled water. Standardize against pure antimony having exactly the same conditions for titration as are specified for the analysis of the alloy. Each cubic centimeter is equivalent to approximately 0.00500 gram of antimony or 0.00465 gram of iron.

Ferrous Ammonium Sulphate.— Dissolve 12.4 grams of ferrous ammonium sulphate crystals in 950 c.c. of distilled water and add 50 c.c. of H_2SO_4 (specific gravity 1.84).

Starch.—To 1000 c.c. of boiling water, add a cold suspension of 6 grams of starch in 100 c.c. of distilled water; cool, add a few drops of chloroform and mix thoroughly.

(a) Determination of Arsenic

In a 300-c.c. Florence flask, dissolve 0.5 gram of the alloy in exactly 8 c.c. of H_2SO_4 (specific gravity 1.84). The metal must be finely divided, preferably in the form of thin foil like shavings, although sawings or very fine drillings may be used. Heat the solution to boiling; cool, add about 5 c.c. of water and a bulk of about 0.5 c.c. of clean granulated pumice stone and boil the covered solution very gently for about five minutes, or until the strong odor of SO_2 can no longer be detected. Finally, being careful to have 5 c.c. of water present, cool the solution to about 18° C. and cautiously add 20 c.c. of HCl (specific gravity 1.20). Insert in the flask a rubber stopper fitted with a thermom-

eter and delivery tube and connect the delivery tube with the "S" condenser. Heat the solution to gentle boiling for from 10 to 15 minutes, keeping the vapor temperature at 107° C. for at least 5 minutes. Wash out the condenser into a 300-c.c. beaker and add an excess of about 2 grams of $NaHCO_3$. Bring the volume of the solution to about 200 c.c.; warm to about 27° C. and titrate with standard iodine solution and starch to the appearance of a deep blue color.

Note.—A blank determination should be made on corresponding amounts of reagents treated as above, and the results should be corrected accordingly.

(b) **Determination of Antimony**

Cool the solution which remains in the flask after the arsenic distillation; add about 130 c.c. of cold, recently boiled distilled water, to which has been added about 3 c.c. of HCl (specific gravity 1.20) and titrate with standard $KMnO_4$ solution to the appearance of a decided permanent pink color. From a burette add an excess of standard ferrous ammonium sulphate solution until the pink color is discharged and then titrate with standard $KMnO_4$ solution to the reappearance of a pink color.

(c) **Determination of Tin**

If the sample does not contain 14 per cent (or 0.07 gram) of antimony, add enough dissolved $SbCl_3$ to the solution to bring the contents of antimony up to about 0.07 gram for the purpose of insuring perfect reduction of the tin and uniform conditions for the titration. Then add exactly 6 c.c.

of H_2SO_4 (specific gravity 1.84) and 60 c.c. of HCl (specific gravity 1.20) and add about 6 in. of clean, soft No. 14 pure iron wire cut into 2 in. lengths and cleaned with dilute HCl just before using. Boil gently for 30 minutes, add about 6 in. more wire and boil 30 minutes longer. Remove from heat, close flask loosely with a rubber stopper and allow about two minutes for all air to be expelled by hydrogen and acid vapors. Close flask tightly and quickly place it in cold water, cooling the solution to about 20° C. Transfer the solution quickly to a 500-c.c. beaker (leaving the iron wires in the flask) and rinse flask and contents with 150 c.c. of cold, recently boiled distilled water. Add rinsings to main solution in the beaker, bring final volume to about 300 to 350 c.c. and titrate quickly with standard iodine solution and starch to the appearance of a strong blue color.

Note.—A blank determination should be made on corresponding amounts of reagents treated as above, and the results should be corrected accordingly.

If the copper content of the alloy is as high as about 3 per cent or over, it prevents a good end point in the tin titration when the tin percentage is low. Under such conditions, just before titrating, add about 1 gram of KI crystals, stir until nearly dissolved and titrate immediately. If allowed to stand too long at this point, trouble may be encountered, due to the precipitation of some of the constituents.

Other forms of pure iron may be employed, but the wire as above specified has been found convenient.

For accurate work it is desirable to reduce and titrate the solution of tin in an atmosphere of CO_2.

CHAPTER XV

PHYSICAL PROPERTIES OF PIGMENTS

Determination of Apparent Density

The determination of the apparent density and fineness of lead compounds has lately become of special importance in many laboratories where it is essential that the physical properties of these compounds be under control. The method must combine accuracy and rapidity. While many methods have been suggested for such control, it has been found that when rapidity is required the most excellent results are obtained through the determination of the weight of a cubic inch of the compound. This weight is dependent on two factors, the fineness and the density of the particles.

The determination is carried out on a Scott volumeter, modified by replacing the funnel having a fixed wire screen, with a funnel having an elongated neck, so arranged as to allow the use of various mesh silk bolting cloth. See Fig. 3. While not only allowing of numerous determinations of fineness, the difficulty encountered through particles of the compound adhering to the wire screen is eliminated.

The apparatus consists of a stand, A, on which is mounted a small tower, B, containing baffle plates of glass which serve to evenly distribute the compound under examination. The funnel is divided into two sections, one the funnel proper, D, and the other the neck, E, which fits over the

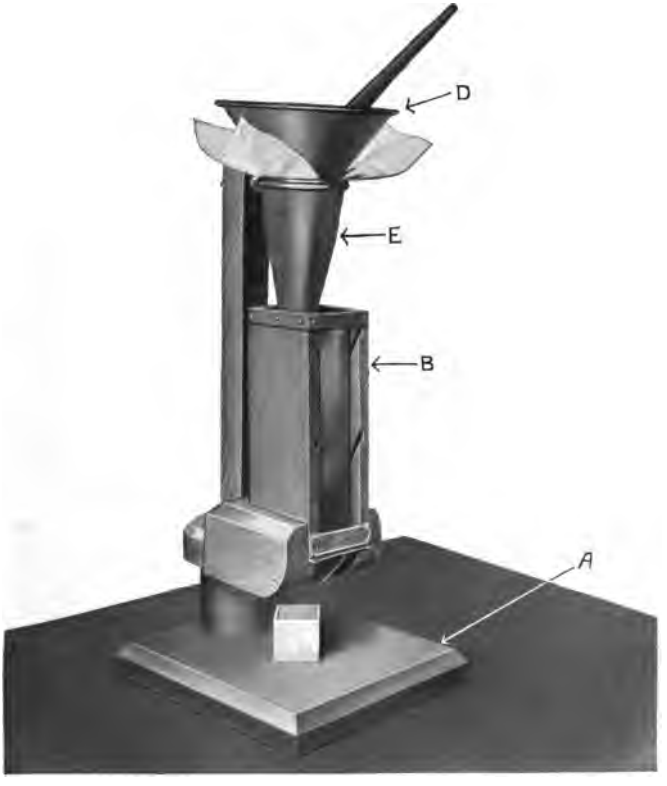

FIG. 3. Modified Form of Scott Volumeter.

funnel proper and holds the silk bolting cloth firmly in place. The metallic cube is exactly one cubic inch in size.

The mesh cloth most suitable for the compound on which the determination is being made is fastened in the funnel. It has been found that a No. 9, Standard Silk bolting cloth which has about 97 meshes to the inch gives concordant results, it being of such coarseness as, in most cases, to allow all the compound to be brushed through the cloth. The cube is placed directly under the baffle plates, the compound is placed in the funnel and gently brushed through until the cube is entirely filled. By a rapid stroke with a spatula the excess of the compound is removed, leaving an even cubic inch of the material. The cube and its contents are then weighed and the weight of the cube deducted, giving the weight of a cubic inch of the compound. Several determinations should be made and an average should be taken. Results may be obtained by this method which vary not more than ½ of a gram. In the hands of different analysts it has been found that results may vary more than this, due to the personal equation in the carrying out of the method; however, the method is only a comparative one and enables any analyst to closely check the apparent density of compounds in a very rapid manner.

The laboratory of the Willard Storage Battery Company has improved the Scott Volumeter by attaching an electric buzzer to the side of the volu-

meter. This buzzer is operated when a gram weight determination is being made and renders results more accurate in that it prevents any of the pigment adhering to the glass baffles.

"Gram Weight."— If the weight of the cubic inch of pigment is determined in grams the result is called the " gram weight" of the pigment.

Color, Color Strength, Coarse Particles

In making determinations of these physical properties of pigments the analyst should use the methods as outlined in the Circular of the Bureau of Standards, No. 85, on "Recommended Specifications for Basic Sulphate White Lead, Dry and Paste," as found on page 15.

Oil Absorption[1]

The oil absorptive property of pigments is a physical property that is often measured and the best results can be obtained only by adhering closely to the method of Gardner and Coleman.[1] A brief summary of the most important details follows.

Weigh 20 grams of dry pigment, free from lumps, and place in a 400-c.c. beaker or round bottom jelly glass. Drop raw linseed oil slowly from a burette onto the pigment, carefully lifting the pigment with a spatula until all the pigment has become wet with oil. Stirring or otherwise bringing pressure to bear on the pigment

[1]Papers on Paint and Varnish, Gardner.

should be avoided. As the end point is approached the pigment will gather in small balls. Finally the small balls will unite in one large one which will flatten out in the bottom of the glass into a sticky mass. This is the end point. The number of cubic centimeters of linseed oil multiplied by five gives the amount of oil required for 100 grams and this is taken as the oil absorption figure.

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